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REFRACTORY GADOLINIUM AND HAFNIUM COMPOUNDS

May 1960

Contract NObs 77145

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RESEARCH CHEMICALS

a division of
nuclear corporation of america
burbank, calif.



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REFRACTORY GADOLINIUM
AND HAFNIUM COMPOUNDS

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RESEARCH CHEMICALS
A Division of Nuclear Corporation of America
Burbank, California

May 1960

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F O R E W A R D

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ABSTRACT

Gadolinium compositions with bismuth, antimony, silicon, boron, phosphorus and selenium, and hafnium compounds with silicon and boron have been examined for their potential as thermoelectric materials. Seebeck potentials, resistivities and melting points have been determined. Several refractory systems have been uncovered, with melting points as high as 3000°C , and compounds in the gadolinium-selenium systems have demonstrated a possible value as a thermoelectric material.

In the gadolinium selenium system Seebeck outputs as high as $500 \mu\text{v}/^{\circ}\text{C}$ have been obtained but this and resistivities have been found to vary unconventionally with treatment and mild variations in composition. "Doping" of the Gd_2Se_3 compound composition with small amounts of copper appears not to have an advantageous effect upon electrical characteristics of the material and a tentative investigation of the chemistry of the system has led to the belief that the value of the gadolinium selenium system for thermoelectric applications depends upon an as yet undetermined relationship between GdSe and Gd_2Se_3 compounds.

* microvolt/ $^{\circ}\text{C}$

INTRODUCTION

This final report describes the work performed during the period May 18, 1959 to May 1, 1960, under Contract NObs-77145 (Index No. SR-010024-1BR) on refractory gadolinium and hafnium compounds. Personnel involved in the work reported included Messrs. E. Avis, W. Lavold, W. C. Sexton, V. Novy, H. M. Muir, L. Thomas and the project leader, Dr. R. C. Vickery. Dr. G. Vineyard has contributed to much of the discussion.

The aims and objectives of the work undertaken have been to investigate compounds of gadolinium and hafnium with other elements which, while attaining a high degree of refractoriness, also are so bonded as to develop a significant output of thermoelectric power at elevated temperatures. Measurement of Seebeck coefficients and resistivities for a group of selected compositions were to be made.

BACKGROUND CONSIDERATIONS

Theoretical aspects of the development of thermoelectric power have been treated by several authorities and do not require iteration here. Of specific concern is the material structure requirement leading to both high temperature stability and the production of an appreciable thermoelectric output.

In the purist sense no direct correlation of these two required parameters can be made. Although several formulae have been presented from which the thermoelectric power of a system can be predicted, such formulae require however the knowledge of precise structural data which are in many instances, lacking. The requirement still exists therefore for examination, on a generalistic basis, of many previously unexamined materials.

Other workers have developed the concept that mixed valence compounds should provide valuable thermoelectric parameters. This interpretation is felt however to be rather ambiguous and a more precise concept is that based upon systems in which bonding resonates between covalent (or homopolar) and ionic characteristics. Such resonance will strengthen the bond and thus increase the melting point of the system and most probably the energy gap. Again, because of the covalent bonding, it is to be expected that such materials will be semiconducting.

For valuable application to thermoelectricity it is

necessary that semi-conductors be extrinsic, since otherwise hole and electron conductance will militate against each other.

Specifically therefore, with the foregoing generalizations in mind, it was pertinent to consider the value of intermetallic compounds as thermoelectric materials. The semiconducting properties of intermetallics are due to the number of states and number of available electrons such that the valence band comprises all the bonding states and that the conduction band is formed by anti-bonding states. This also means that the chemical stability of the system must be higher than that of a metal phase. This stability is of course further increased by the covalent - ionic resonance and increase in the energy gap.

Of direct importance in determining the value of a material for thermoelectric purposes is electrical resistivity. It has long been known that resistivity shows a sharp increase at compositions satisfying simple chemical valence rules and that the structure of such compositions is not metallic. We would therefore, appear to be constrained, in the generalistic sense, to examination of intermetallic compounds in which ionic - covalent resonance occurs in non-stoichiometric compositions, and in which conduction is electronic rather than ionic, the whole system being also an extrinsic semiconductor. Through a constitutional series however, it is also noted that

resistivity will vary with the degree of order-disorder obtaining and hence low resistivities are to be expected where non-stoichiometric intermetallic compounds are formed. In the work now reported, wide spans of composition have not however been made, arbitrarily chosen compositions only having been studied.

It was suggested that the required parameters of resistivity, Seebeck e.m.f. and refractoriness might be met by compositions involving the rare earth metals. From the electrical stand-point, the rare earth elements are interesting since their electron transport properties are related to the strongly shielded 4f electron component. In the rare earth series per se, gadolinium is of specific interest because its 4f shell carries the maximum number of unpaired electrons. However, considering also the end of the rare earth series, lutetium has 14 4f electrons. The rarity of this element however, induced consideration of the next member of the Periodic System - hafnium, which also carries 14 4f electrons and an additional electron in the 5d shell.

Consequently work has centered on studies of the thermoelectric propensities of gadolinium and hafnium with selected elements to the right of the Zintl boundary in the Periodic Table. Boron compounds have also been examined.

In general some correlation of data has been obtained

with previously established theoretical concepts, but some apparent anomalies have also been observed. These comparisons and discrepancies will be considered later.

In the studies now reported, Seebeck coefficients, electrical resistivities and melting points only, have been determined for the materials prepared. It is accepted that these alone cannot determine the value of a material for thermoelectric purposes. Such a criterion can only be ascertained by considering the "figure of merit" - Z - which relates Seebeck coefficient, resistivities and thermal conductivity. Assuming that, for non-anomalous states, the Weidemann-Franz ratio holds and that the Lorentz number will relate thermal and electrical conductivities, it might be considered convenient to accept the free electron model which gives $KR = LT$ (where L is the Lorentz number). This does not however, give accurate results for intermetallic compounds since bonding type affects both lattice and electron conduction. Moreover, because in at least one instance, the work reported dealt with a very "poor" metal, lattice thermal conductivity will be appreciable and the Weidemann-Franz law applies only to the electronic (or non-lattice) part of thermal conductivity. Because of this, no attempt has been made herein to employ the above relation directly.

In the work reported therefore, only Seebeck coefficient, electrical resistivity values, melting point, and general

chemical stability have been considered in order to effect a preliminary screening of materials in preparation for a subsequent deeper investigation of the more promising compositions.

EXPERIMENTAL

Component Materials. Materials employed in the preparation of the refractory compositions considered in the work reported have been..

- A. Gadolinium
Research Chemicals 99.7%
- B. Hafnium
Wah Chang Corp. electron beam
ingot grade
- C. Bismuth
Baker & Adamson 99.9 %
- D. Antimony
Ohio Semiconductors, Inc. electronic
grade 99.999 %
- E. Silicon
Dupont Company - Solar cell grade
99.999 %
- F. Boron
U. S. Borax Corp. Crystalline
boron 99.9%
- G. Phosphorus
Baker & Adamson 99.9 %
- H. Selenium
American Smelting & Refining Co.
99.999 %
- I. Zinc phosphide
Fisher, technical grade, redistilled
by Research Chemicals to 99.9%
- J. Calcium phosphide
Baker & Adamson, technical grade

Material Preparation Procedures. Four types of reaction procedures have been employed for the preparation of polycrystalline, refractory gadolinium and hafnium

compositions. These techniques were direct reaction, vapor diffusion, arc melting and, in phosphide production, metathesis.

A. Direct reaction

The two material components were reacted together in an inert argon atmosphere, induction heating being used to trigger the initial reaction. Once the critical reaction temperature of the composition under study had been reached, the heat of reaction of the components supplied the final heat required to complete the reaction.

Spun tantalum crucibles 0.030" thick x 1 1/2" o.d. x 2" high were used as containers. A Kinney F-9 high vacuum induction furnace was employed as the heating source and the inert atmosphere reaction chamber. The materials to be reacted were blended together and packed loosely into the spun tantalum crucible which was fitted with 0.003" thick tantalum splash covers to prevent loss of material during the violent exothermic reaction occurring at the critical temperature. The charged crucible was inserted into a 0.030" x 5/8" o.d. x 6" high tantalum susceptor positioned in the Kinney furnace.

In operation, the furnace was evacuated to 50 microns pressure from which point two argon purges were performed. The furnace was then back filled with argon to a pressure of 10 p.s.i. At this point, induction heating was commenced, and continued until the critical reaction

temperature, specific for the system was reached. At this point, violent exothermic reaction was observed and power input to the induction coil immediately stopped. The heat of reaction then supplied the heat necessary for the reaction to go to completion.

Two factors militated against general use of the foregoing technique. Products formed in this manner were inhomogeneous and, for the most part, the melting points of the systems being examined were in excess of the operational temperature range of the Kinney F-9 Furnace, (1650 to 1700°C) so that no reconsolidation melting could be effected. Another method for forming homogeneous compositions of these refractory materials was therefore required and the non-consumable tungsten electrode arc melting procedure (C below) was examined as an alternative. No success was achieved in attempting to prepare gadolinium phosphide by this procedure.

B. Vapor Diffusion Reaction

Because of the high vapor pressure of phosphorus and selenium, the gadolinium-phosphorus and gadolinium-selenium compounds required for study could not be prepared directly by the technique described above. A vapor diffusion technique was therefore developed for the selenium bearing system. The products of this technique were subsequently homogenized by the standard arc melting process. Phosphides were prepared only by metathesis (D. below)

since in their attempted preparation by vapor diffusion violent explosions occurred even at low heating rates.

Vapor diffusion reaction was effected in a length of Vycor tubing ($1/2$ " o.d., $1/16$ " wall). After sealing one end of the tube, gadolinium metal was introduced in the form of chips of approximately $1/32$ " cube size. A constriction was then drawn by melting the tube above the metal layer and selenium in $1/16$ " diameter pellets was introduced above the constriction. Direct, solid contact of the reactants was thus prevented. After evacuating the system to 3-5 microns pressure, the open end of the tube was sealed off and the whole inserted into a $1\ 1/2$ " o.d. tube combustion furnace.

Furnace temperature was then slowly increased, at approximately 100°C/hr , up to 900°C . This temperature was maintained for 24 hours when power input to the furnace was discontinued. The system then cooled to room temperature at approximately 200°C/hr .

By enforcing a slower rate of reaction, and hence better control, this technique also avoided the explosive reaction which occurred when the gadolinium-selenium systems were reacted directly in either the induction or arc furnace. Once formed by this diffusion reaction, the intermetallics could be remelted in the arc without further danger of explosion.

From the diffusion reaction, gadolinium-selenium

compounds were obtained as powders. These powders were consolidated and homogenized by blending and pelletizing at 10,000 to 15,000 p.s.i. The resultant pellets, approximately 1 1/4" diameter x 1 1/2" thick were then fused by the standard arc melting process.

C. Arc Melting

The arc melting procedure was conducted in a furnace consisting of a water cooled vacuum chamber fitted with a water cooled copper hearth plate and a 1/4" o.d. tungsten electrode. Copper molds approximately 1" to 1 1/4" o.d. x 1/2" high, positioned on the copper hearth plate, were used as material containers during the melt, and viewing ports permitted observation during the melting process. The furnace was evacuated to 50-100 microns and purged twice from this point with a 75% helium, 25% argon mixture. The system was back-filled with the helium-argon mixture to a pressure of 25 mm Hg before proceeding with the arc melting operation.

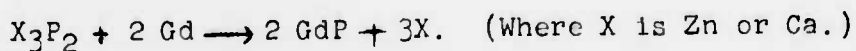
The tungsten electrode was positioned to a gap of approximately 1/16" and arcing initiated through a high frequency starter. The electrode was then manually positioned to establish a voltage potential of approximately 30-60 volts and the current increased to 200-400 amps depending on the material being melted. Current was maintained and the electrode manually manipulated with a circular motion until the entire mass became molten. The average

heating cycle for the gadolinium and hafnium containing systems was approximately 1 to 2 minutes per melting operation.

The ingot was cooled to room temperature before examination and the arc melting cycle was repeated 2 to 3 times with the ingot being inverted between each melt to insure a homogeneous structure.

D. Metathetical Reaction

Although previous studies on gadolinium phosphide reported its preparation by direct reaction, the present work has been unable to confirm this and the closest approximation obtained to the gadolinium phosphide composition was through the metathetical reactions.



The zinc phosphide reaction was preferably employed because of the relative ease with which the zinc metal product could be removed by distillation. Experimental studies on this procedure were as follows:

(i) Double Decomposition Sintering (Argon Atmosphere)

Fine gadolinium turnings and powdered zinc phosphide (Zn_3P_2) were lightly packed into a 0.040" tantalum crucible (2" o.d. x 1" high) covered with a 0.003" tantalum cap. The charge was placed into a tantalum susceptor in a Kinney F-9 induction furnace. The furnace was then evacuated to 100 microns at which point it was purged with argon.

The system was again evacuated to 100 microns and then back filled with argon to a pressure of 15 p.s.i. The temperature of the charge was next slowly raised to approximately 1100°C at which point an exothermic reaction took place. Heating was continued until 1500°C was reached at which point the power input was ceased and the charge allowed to furnace cool in the argon atmosphere.

The reacted phosphidic composition from this procedure was then pulverized in an argon atmosphere until all material passed 200 mesh. This product was then pressed into a 1" o.d. x 1/4" disc under 8,000 to 10,000 p.s.i.

The pellet obtained was placed on a 0.003" tantalum sheet inside a tantalum susceptor and again set up in the Kinney F-9 induction furnace. The furnace was evacuated to 100 microns and purged with argon from this point. Another evacuation of the system to 100 microns was followed by a back filling to 15 p.s.i. with argon before starting the sintering cycle.

The heating input was adjusted to raise the temperature to 1500°C in two hours. After a one hour soak at this temperature, the input was stopped and the gadolinium phosphide pellet allowed to furnace cool at approximately 800°C per hour.

(ii) Double Decomposition Sintering
(200 to 500 Microns)

This procedure was similar to that used above. The pressure however, was reduced to 200-500 microns rather

than the 15 p.s.i. argon atmosphere. Identical heating rates were used and at approximately 1100°C the exothermic reaction was again observed. Heating was continued up to 1500°C and full mechanical vacuum maintained throughout the reaction. Power input was controlled to maintain the temperature of 1500°C for approximately 1/2 hour after which time the product was allowed to furnace cool at approximately 200°C per hour.

The material was then treated in the manner previously described in (i) except that sintering was carried out at 200-500 microns pressure.

(iii) Double Decomposition (200-500 Microns) followed by a vapor reaction.

In this procedure, an attempt was made to increase the phosphorus content of the product by applying a vapor reaction technique to a gadolinium-phosphorus composition previously prepared by the double decomposition procedure. It was hoped that a vapor reaction might be thus carried out without the explosions previously experienced.

A phosphidic product was prepared using the double decomposition reaction carried out at 200-500 microns pressure (ii, above). Chemical analysis on this product showed it to contain 11.1% phosphorus.

This material was then pulverized and screened, in an argon atmosphere, until all material passed 200 mesh. The product was then blended with zinc phosphide powder in

amount calculated to give a 3% excess phosphorus content. The blended materials were then sealed into a Vycor tube and a standard vapor diffusion technique started. Temperature was raised slowly in increments of 50°C per two hours. Temperature had attained, and been maintained at, 200°C for approximately two hours when a violently explosive reaction occurred. The reaction product was recovered and separated from the pulverized Vycor contaminate. Analysis of this material showed it to contain 12.5% phosphorus or approximately 1 1/2% phosphorus increase over the previously 11.1% phosphorus in the original double decomposition product.

(iv) Double Decomposition Reaction Employing Distilled Zinc Phosphide

The zinc phosphide employed in the double decomposition reaction was a Fisher, technical grade product, and chemical analysis showed it to contain only 85% zinc phosphide as Zn_3P_2 . Purification of this material was effected, without difficulty, by vacuum distillation and a product containing 99.9% Zn_3P_2 was obtained. Using the distilled zinc phosphide, a double decomposition reaction was carried out followed by vacuum sintering of the product. Analyses showed the reaction product to contain only 8.44% P instead of the required 16.5%.

A product of slightly higher phosphorus content was obtained by using calcium phosphide in a double decomposition reaction. The reaction was carried out in

vacuum followed by vacuum sintering. 19.6% calcium contaminated the product however.

Analytical Procedures. Techniques employed for determination of chemical composition of materials prepared have followed classical techniques.

Gadolinium-antimony compositions were dissolved in aqua regia, the antimony precipitated as the sulphide by use of hydrogen sulphide and finally determined iodimetrically. Gadolinium in the antimony free solution was then precipitated as oxalate and determined gravimetrically after ignition to oxide.

Bismuth containing compositions were dissolved in hydrochloric acid, the bismuth content hydrolysed as the oxychloride and weighed as such. Gadolinium was determined gravimetrically as above.

Selenium was determined in gadolinium-selenium compositions after fusion of the sample in sodium-potassium carbonate mixture, by precipitation with sulphurous acid and weighing finally as the metal. Gadolinium was determined gravimetrically in the filtrate.

Silicon alloys with gadolinium were decomposed by fusion with sodium peroxide, the melt taken into solution with dilute hydrochloric acid and evaporated to dryness to insolubilize the silicon as silicon dioxide which was then determined gravimetrically.

Gadolinium-phosphorus compounds required dissolution

in nitric acid under reflux conditions and a bromine trap to ensure that no loss of phosphine occurred. In the final solution, phosphorus was determined volumetrically with ammonium molybdate and gadolinium by gravimetry.

Boron containing gadolinium systems were decomposed under reflux in the same way as gadolinium-phosphorus compositions, and the boron content titrated with standard alkali after the addition of mannitol.

Hafnium-silicon compositions were treated similarly to the gadolinium-silicon alloys, silicon being determined gravimetrically as silicon dioxide. Where hafnium contents were required, precipitation with diammonium phosphate was followed by ignition to, and weighing of, the hafnium pyrophosphate.

Hafnium-boron systems were treated identically to the gadolinium-boron systems except for the addition of hydrofluoric acid during the decomposition step.

Sample Preparation. All of the refractory hafnium and gadolinium compositions prepared were found to be hard and brittle which presented some difficulty in preparing specimens suitable for the required resistivity and Seebeck evaluations. Several grades and thicknesses of silicon carbide cut off wheels were employed in the initial specimen preparations with varying degrees of success depending upon the refractory system being fabricated. A general purpose cut off wheel suitable for all materials-cutting requirements

was later developed, consisting of a 100 mesh silicon carbide powder bonded in a rubber base matrix. The wheel had a thickness of 0.030" and satisfactory preliminary fabrication of materials was then possible by its use.

After rough cutting of the specimen to approximately 1.27 x 0.64 x 0.64 cm several polishing steps were conducted. In order to eliminate any surface effect interference, a final polish of specimen was carried out on a 600x emery cloth immediately before the electrical tests were conducted.

MEASUREMENTS

Seebeck Coefficient Measurement. Samples of approximately 1.27 x 0.64 x 0.64 cm dimensions were placed with their polished sides between two platinum plate electrodes which were maintained in firm contact with the specimen by pressure from externally spring mounted stainless steel rods. The whole unit was contained in a Vycor tube through which argon passed continuously during the heating and cooling cycle.

An alumina thermo-couple sheath containing a 20 guage chromel/alumel thermo-couple was inserted through the center of each stainless steel rod and extended to the platinum electrodes. A separate cold junction was used for each thermo-couple employed for measuring the temperature gradient of the sample. The heat source was a nichrome wire wound heater assembled around the Vycor tube.

The platinum electrode system functioned satisfactorily at temperatures up to 1000°C and showed no evidence of contamination from any system examined.

A switching circuit was provided to allow the rapid routing of both chromel/alumel thermo-couples as well as the Seebeck emf to a Kintel, model No. 204A electronic galvanometer. Accuracy of the Seebeck measurements made was felt to be $\pm 10\%$. Figure 1 shows the diagram and electrical schematics for this apparatus.

Resistivity Measurements. The brittle nature of many of the systems being investigated resulted in the disintegration of their fabricated ingots into relatively small samples. Where resistivity values are not reported therefore, it is to be taken that specimens were too brittle to permit fabrication into the required geometry. As indicated above, a sample size of 0.5 x 0.5 x 0.3 cm was selected as the maximum sample size producible for several of the more brittle systems, and it is for this reason that the resistivity measurement apparatus (Figure 2) was so scaled.

The sample, inserted into a 0.9 cm i.d. Vycor tube was seated firmly against four externally spring mounted stainless steel electrodes (0.08 cm o.d. with a 0.00 " ground point). The two outer electrodes (current) were spaced 0.53 cm apart and the inner electrodes (emf) at 0.16 cm. Current in the 100-200 milli-amp range was supplied to the sample by dry cell batteries and measurements were made using a Kintel No. 204A electronic galvanometer. Accuracy of $\pm 5\%$ is felt to have been obtained with contact resistance negated by this procedure since comparable resistivity values were obtained on standard materials.

A non inductive Kanthal wire heater was used as the heat source, maintained to $\pm 1^\circ\text{C}$ over the entire temperature range, through a Wheelco control unit. The heating chamber was purged with argon gas throughout the entire cycle, and no contact contamination was observed from any

system up to temperatures of 1000°C.

Despite the specific accuracy claimed above for measurements, resistivity values must always be regarded conservatively unless monophase, homogeneous materials are being examined. No claim can be made in the work now presented for absolute physical integrity of specimens, hence undetected voids, cracks and other imperfections, may lead to erroneously high resistivity values. Again, because compositions only have been examined in this initial study, without the benefit of structural X-ray studies, it cannot be assumed that each sample was monophase; indeed, the converse is probably more correct. Competing order - disorder transitions may therefore present another source of error.

Melting Point Measurements. The apparatus employed to determine the melting points of refractory compounds consisted of a water cooled gas-tight chamber fitted with two 1 1/2" o.d. quartz view ports, and two adjustable 1/4" o.d. water cooled tungsten electrodes with chamfered ends, (Figure 3). The sample was placed as a resistor between these electrodes which were positioned level with the quartz view ports. Current up to 200 amps, rheostatically controlled, was passed through the sample to effect melting and an optical pyrometer, "sighted in" on the melting zone, was used to measure the melting points. With the reservations indicated below, this apparatus appears capable of determining

melting points of ca 3500°C with an estimated accuracy at this level of $\pm 50^\circ\text{C}$.

The refractory sample (approximately 1/8" cube) was securely wedged between the chamfered electrode tips to ensure good electrical contact. The chamber was then evacuated to approximately 200 microns and two argon purges were made. After back filling the chamber with argon to a slight positive pressure (25 mm mercury), power was applied to the specimen at a uniform rate and the temperature increase measured continuously up to the melting point of the material to ensure the best possible accuracy at the instant of melting. This was determined as the point at which the specimen consolidated as a globule and usually dropped from the electrode contacts.

Some reservations must however be made for the absolute validity of data obtained by this procedure since it does not compensate for thermionic emission or radiative effects. Interanally it has been found preferable to consider melting point data thus obtained as indicative only and to check apparently anomalous data by induction heating conjointly with a reference "black body", of drilled graphite, as pyrometer sighting location.

EXPERIMENTAL RESULTS

Gadolinium-Antimony System. Gadolinium-antimony compositions were prepared at first by the direct reaction technique, followed by arc melting. In later work however, preparation was effected by the arc melting technique only. Materials prepared by both methods appeared to be identical within the measurement error of $\pm 10\%$ based upon standardization of Seebeck emf against Pt-Pt 13% Rh as the reference material.

Tables I and II list the physical, chemical and electrical data determined. Seebeck output values are also shown graphically in Figure 4. Because of sample disruption it was not found possible to assemble a complete resistivity-composition plot, but from the data obtained, it would appear that the 3:2 composition represents a disordered phase since the higher resistivities in this region cannot be justified in terms of valence compositions. Resistivity values between 140 and 300 microhm-cm obtain through the system at room temperatures and the relationship of room temperature resistivity and melting point to composition is shown in Figure 5. Figure 6 relates resistivity to temperature and composition. It is clear from the melting point curve that a complicated band structure exists in alloys of the gadolinium-antimony system. The relatively low values for Seebeck coefficients and the high electrical conductivities

would seem also to confirm that the bonding is complex and semi-metallic. The few anomalies apparent in variation of Seebeck coefficient with temperature may be attributable to overlap of conduction and valence bands by impurity bands. Because it is obvious from the peaking of resistivities at ca 30% antimony that a degree of ionic binding is present, crystal defects in the samples may also function as impurities.

Gadolinium-Bismuth System. Gadolinium-bismuth compounds were initially prepared using a combination of the direct reaction procedure followed by arc melting. However, as in the gadolinium-antimony system, a second series of gadolinium-bismuth compositions was prepared using the arc melting technique. Analysis of products of both methods of preparation indicated identity of composition.

Tables III and IV and Figures 7, 8, and 9 present the data obtained in this system.

The relatively smooth curve for melting points in this system suggests a simple variation in energy gap with average molecular weight; the steep increase in resistivity at ca 50% gadolinium suggests however, the development of a high degree of ionic bonding in this area and it is possible that, as well as the stoichiometric GdBi at 42.6% Gd, a Gd_5Bi_3 exists at 55.2% Gd, with the bismuth moiety assuming its pentavalent state. Although the range of resistivity values attained with compositional change is not wide, ca 150-500 microhm-cm at 30°C, nevertheless the variations which

do occur are in keeping with the above concepts as well as with the probability that GdBi_2 exists as an ordered inter-metallic structure. The general instability of compositions in this system - rapid oxidation and hydrolysis--militates however against their further consideration in the present context.

Gadolinium-Selenium System. Compositions in the gadolinium selenium system were prepared by the vapor diffusion reaction technique, followed by arc melting to improve physical homogeneity. Tables V, VI and VII and Figures 10 to 15 present the experimental data obtained on these systems.

Because of the highly significant Seebeck emf's and resistivities obtained through this series (up to 700 microvolts/ $^{\circ}\text{C}$ and as low as 219 microhm-cm respectively) a deeper study was made of the processing variables in this system, the extent and value of doping with copper and the preparation chemistry of the materials. The chemistry of that part of the system examined has been presented in a paper submitted for publication and reproduced here as the Appendix.

It would seem significant that the gadolinium-selenium system is the only one studied which presents resistivity values of any magnitude. Also, it is the only system attaining high Seebeck coefficients. The moderate tendency for resistivities to parallel thermal emf (Tables VI & VII)

is suggestive of simple model semiconductor characteristics. These will be considered further in the final discussion.

In earlier work which had produced materials of low resistivity and high Seebeck output, copper had been found present in concentrations above "trace" levels; doping with this element was therefore examined since it was suspected that Gd_2Se_3 in stoichiometric single phase would be an intrinsic semiconductor and hence valueless for thermoelectric purposes. However, with copper present, an excess of "vacancies" would develop which would reduce lattice thermal conductivity by increasing phonon scattering.

Later work showed this assumption of the value of copper to be incorrect and that the major influence in this area appears to be that exerted by the GdSe compound and its association with the stoichiometric Gd_2Se_3 . Because of this and earlier lack of knowledge of the phase construction of the gadolinium-selenium system, attempts to correlate resistivity with composition are abortive. Further studies should be made of the gadolinium-selenium system and the interrelationship of its thermoelectric value with $\text{GdSe}/\text{Gd}_2\text{Se}_3$ ratio.

The effects of copper and processing variables are shown in Tables VI and VII, the data for which were derived on the following basis:

A 400 gram batch of vapor-reacted Gd_2Se_3 material was prepared and thoroughly blended to insure a

homogeneity so that comparative values might be obtained for the entire processing evaluation.

The following list indicates the variable parameters examined:

- A. Vapor reacted material sintered at 1500°C in a 5 p.s.i. argon atmosphere.
- B. Vapor reacted material sintered at 1500°C in a 200 micron atmosphere.
- C. Vapor reacted material arc-melted on a copper hearth plate.
- D. Vapor reacted material with 0.1% copper added sintered at 1500°C in a 5 p.s.i. argon atmosphere.
- E. Vapor reacted material 0.5% copper sintered at 1500°C in a 5 p.s.i. argon atmosphere.
- F. Vapor reacted material 1% copper sintered at 1500°C in a 5 p.s.i. argon atmosphere.
- G. Vapor reacted material 0.5% copper sintered at 1500°C in a 200 micron atmosphere.
- H. Arc melting on a tantalum hearth plate of a vapor reacted material sintered at 1500°C in a 200 micron atmosphere.
- I. Vapor reacted material melted in tantalum in a 5 p.s.i. argon atmosphere.
- * J. Vapor reacted material, cast in graphite.
- * K. Vapor reacted material, sintered at 1400°C in argon.
- * L. Vapor reacted material, sintered at 1600°C in argon.

- ** M. Vapor reacted material, arc melted.
- ** N. Vapor reacted material, cast in graphite.
- ** O. Vapor reacted material, hot pressed.
- P. Vapor reacted material, arc-melted (Gd_2Se_3)
- Q. Vapor reacted material, arc-melted (Gd_3Se_4)
- R. Vapor reacted material, arc-melted (GdSe)
- * J. K. & L. material prepared with 3% excess selenium present during vapor-solid reaction.
- ** M. N. & O. materials prepared with stoichiometric ratios present during vapor-solid reaction.

In absence of classical metallographic and X-ray studies on these materials, no direct correlation can be made of electrical characteristics with composition. However, assuming, possibly invalidly, that the material studied represented a homogeneous phase, it would appear that resistivity values can be increased by sintering or arc melting the vapor-reacted composition. When this treatment is conducted in vacuum, Seebeck outputs of the products also increase - possibly due to minor loss of volatile components.

Copper "doping" between 0.1 and 1% has little or no effect upon Seebeck coefficient or resistivity. Although selenium, in excess over stoichiometry during initial reaction, would seem to increase both Seebeck and resistivity values, in general, mild variations in composition from that of 2:3 compound lead to both lower Seebeck coefficients and resistivities.

Gadolinium-Silicon System. The direct reaction procedure only was used in this series of preparations. Arc melting was unnecessary as the melting points of the compounds formed were sufficiently low that complete melting was attained in the Kinney F-9 furnace with direct formation of homogeneous ingots.

Tables VIII and IX list the data obtained for compositions in the gadolinium-silicon system. Seebeck outputs (20-30 micro volts/ $^{\circ}\text{C}$) are also shown in Figure 16. Plots of resistivity vs composition and temperature (Figures 17 & 18) show clearly the development of ionicity at the stoichiometric composition Gd_4Si_3 . Resistivity values (900 microhm-cm at 200°C) for this composition exceed those of adjacent compositions by factors of two or three and Seebeck outputs are lower at this composition. The smooth variation in melting points (Table VIII) indicates a simple band structure.

Gadolinium-Phosphorus System. As indicated above, we were unsuccessful in preparing the 16.5% P (GdP) composition required for examination. The several processing techniques employed have been given previously. Table X and Figures 19 and 20 compare composition with Seebeck output and resistivity data at varying temperatures. Because of obvious impurity levels however no attempt has been made to establish a theoretical assessment of the system. The gadolinium-phosphorus system in the low phosphorus range appears very stable and refractory with melting points ranging from

1900 - 2800°C depending upon phosphorus content.

Gadolinium-Boron System. The two compounds required for this system, (GdB_4 and GdB_6) were prepared using the standard arc melting procedure. The buttons were each melted three times to ensure a homogeneous structure. Data obtained on this system are reported in Tables XI and XII and Figures 21 and 22. It can clearly be seen that while Seebeck outputs for both systems are almost identical, the hexaboride has a much lower, low temperature resistivity than the tetraboride.

Hafnium-Silicon System. Compounds in this system were also prepared using the standard arc-melting procedure, homogeneity of structure being ensured by melting each composition 2 or 3 times. Data obtained are shown in Tables XIII and XIV and Figures 23 and 24. Resistivities seem generally to decrease with increasing silicon content but until the HfSi_2 composition is reached, this has no effect upon Seebeck output.

Hafnium-Boron System. Compounds were prepared using the standard arc-melting procedure. Due to its highly refractory nature, considerable more difficulty was encountered in arc melting the hafnium-boron system than in the hafnium-silicon system. Three to four melts were required to form homogeneous structures suitable for examination. Table XV and Figure 25 present data obtained which show consistent but low Seebeck output values. Brittleness prevented determination of most resistivities.

DISCUSSION

Attention will be devoted, in this discussion, to the observations on electrical properties. Examination of the tables and graphs reveals that most of the materials considered have electrical resistivity and Seebeck coefficient values in a range which is rather common for semi-metals and semi-metallic compounds -- about 30 to 500 microhm-cm for the resistivity and perhaps 10 to 30 microvolts per degree C for the Seebeck coefficient. The magnitudes of both of these quantities are consistent with a situation in which a conduction band contains a very considerable number of carriers, but not as many as in an ordinary metal. This could be brought about by overlapping of valence and conduction bands, or by a very heavy degree of doping from impurities, lattice imperfections, and lack of stoichiometry. In any of these cases the Fermi energy would lie in a region with a fairly high density of electronic states and thus would not shift rapidly with temperature. The temperature dependence of the resistivity would be dominated by the decrease of carrier mobility (causing an increase of resistivity) with temperature. An increase of resistivity with increase of temperature is observed in almost all cases, (Gd_2Sc_3 is an exception which will be considered below). The dependence of Seebeck coefficient on temperature is more complex because there is an opposition between the contributions of positive and negative carriers. With carriers of

DISCUSSION

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both signs present, as there may well be in many of these specimens, complicated shifts of compensation with temperature would be expected. The experimental results yield no obvious systematic trend in the variation with temperature, which is in accord with this argument.

It should be noted that the purity obtained in these refractory materials is very low by the standards of modern semiconductors, and the variability between specimens of the same nominal composition is high.

From an electrical and thermoelectric standpoint, the most interesting substance uncovered is gadolinium selenide and there is evidence that this material should be classed as a semiconductor. The most striking difference between it and all the other materials investigated here is the high resistivity and higher Seebeck coefficient. The former is higher by one to three orders of magnitude, and the latter is higher by about one order of magnitude. Reasons why this material should be more of a semiconductor than the others are not entirely clear, although it should be noted that the composition corresponds to the principal valence of both ingredients.

Among the various samples of gadolinium selenide there is also a tendency for the samples of higher resistivity to have higher Seebeck coefficients. One example is the pair of specimens P and R. Also the highest resistivity of all in specimen J (1 ohm-cm at 200°C) and this had one

of the highest thermoelectric powers (500 micro volts per degree at the same temperature). Although it is quite impossible to infer the band structure of this material from such limited data, and although its very low purity and polycrystallinity make it risky to push too far an analysis in ordinary semiconductor terms, it is suggestive to consider a simple semiconductor model in comparison with these results. Thus, consider a semiconductor in which one kind of charge carrier, moving in one band, predominates. If this carrier has mobility μ , and is present, at temperature T , in concentration n (carriers per unit volume), then the electrical resistivity ρ is given by

$$\rho = \frac{1}{en\mu} \quad (1)$$

Here e is the charge on an electron. If it is also assumed that the predominant scattering mechanism leads to a mean free path for the carriers ℓ related to the kinetic energy of the carrier ϵ by the law

$$\ell \sim \epsilon^r \quad (2)$$

where r is an exponent characterizing the scattering, the Seebeck coefficient α is given by

$$\alpha = \pm \frac{k}{e} \left\{ r + 2 + \ln \left[\frac{2(2\pi m^* kT)^{3/2}}{h^3 n} \right] \right\} \quad (3)$$

Here k is Boltzmann's constant, h is Planck's constant, and m^* is the effective mass of the carriers. The sign in front of this expression is determined by whether the carriers are p or n type. Note that $\frac{h}{e} = 86 \mu V/^{\circ}C$ which indicates the general scale of Seebeck coefficient. The scattering law (2) gives mobility proportional to $T^{-3/2}$, so equation (1) can be rewritten now as

$$\rho \sim \frac{1}{enT^{-3/2}} \quad (4)$$

Equation (3) shows that, other things being equal, the Seebeck coefficient increases with lowering of carrier density, n . This is precisely why metals have very low Seebeck coefficients and semiconductors generally have relatively high coefficients. In a simple semiconductor the carrier concentration at a given temperature varies enormously with level of doping (or purity). Equation (4) shows that this may make a very large difference in resistivity, and since n^{-1} enters resistivity, ρ , directly, whereas it enters Seebeck coefficient, α , only under a logarithm, the variation of resistivity with doping will be much more rapid than the variation of Seebeck coefficient.

It is now a plausible hypothesis that the chief difference in the different specimens of gadolinium selenide is the effective value of n , caused by differences in purity (structural as well as chemical). One notices that the

range of resistivity between different specimens is much larger than the range of Seebeck coefficient. Also the tendency of resistivity and Seebeck coefficient to be large in the same specimens is explainable in this simple fashion.

The temperature dependence of electrical resistivity arises because both n and μ (equation 1) vary with temperature. In typical extrinsic semiconductors, the most important dependence is in n , which increases with temperature approximately like an exponential of $-E/kT$ where E is an activation energy. In highly doped or extrinsic semiconductors, on the other hand, n changes much more slowly with T , and μ , which generally decrease* with increasing T , can dominate, causing a net increase of resistivity with T . This may be what is occurring in some of the specimens of gadolinium selenide reported on here.

The temperature dependence of Seebeck coefficient, in the simple model, arises because of the temperature dependence of n (and also possible of r), as well as from the explicit appearance of T in equation (3). There are thus many possible trends, and the data presented do not seem to have a simple interpretation.

* With the scattering law (2), $\mu \sim T^{-r-3/2}$. Mobility will then decrease with increasing T unless $r \geq 3/2$. Such large values of r occur with scattering by impurity ions, but in no other important case.

In addition, it must be remembered that the simultaneous presence of carriers of opposite sign complicates the theory of Seebeck coefficient and introduces further possible variability. Impurities and imperfections, the bands themselves are altered by the impurities and a simple semiconductor model, which assumes (rigid) bands subjected to varying degrees of filling, is inapplicable. In the absence of proof of the existence of this situation, it seems best to attempt to correlate observations with simple models. Pursuing this course to a satisfactory conclusion, however, will require more work to produce material of high and controllable purity, and measurements of other parameters, particularly Hall effect and optical properties.

On a more phenomenological basis also, it is clear that much has yet to be done to determine the precise compositions or compounds in the gadolinium-selenium systems, which yield optimum thermoelectric parameters. For example it has been shown that a variation of ca 0.5% selenium from the Gd_2Se_3 composition reduces by some 75-80% the output obtained from the 2:3 compound.

Again, it would seem significant that, in the gadolinium-selenium system, maximum thermoelectric voltages are obtained at or near the composition equivalent to Gd_2Se_3 . The significance is associated with contemporary magneto-structural studies in these laboratories wherein it has been found that 2:3 intermetallic compounds of the rare earths which adopt

large cubic cell lattices present "anomalous" variations in properties. For example Gd_2Fe_3 and Gd_2Co_3 have large cubic cells and present high maxima of magnetic moments. No Gd_2Ni_3 compound exists and at this composition in the gadolinium-nickel alloy system magnetic moment is vanishingly small. Similar "anomalies" have been found in other rare earth systems and much interest is being evoked in these laboratories aimed at developing a structural theory to account for these phenomena.

If one considers "normal" rare earth compounds such as R_2O_3 , $\text{R}_2(\text{SO}_4)_3$, $\text{R}_2(\text{CO}_3)_3$, etc., the bonding type is found to be almost completely ionic. In rare earth metalloid systems a newer type of bonding occurs which is almost purely covalent except when 2:3 compounds can be prepared and here, when a cubic structure obtains, the bonding appears almost to "resonate" between ionic and metallic i.e. one R-M bond will be metallic and another ionic. Such a "mixed" bond system will inevitably involve different orbital levels and, must therefore have marked effects upon electron interactions, energy levels and bond widths. Full elucidation of theory is as yet incomplete and indeed the hypothesis may be immature, nevertheless, sufficient is known to suggest that cubic 2:3 compounds may present characteristics completely variant from "norm" behavior.

Such a variation may be structurally responsible for the significant Seebeck and resistivity values found for

the Gd_2Se_3 compound.

Again in contemporary studies, indications have been found that replacement of gadolinium in gadolinium selenide by other lanthanons will lead to increased values for Seebeck coefficient and resistivity with increase in atomic weight. Refractoriness would also appear to increase similarly. No data have been obtained on e.g. Sc_2Se_3 or Y_2Se_3 and it is felt that for fuller appreciation there should be examined the replacement of gadolinium in gadolinium selenide by other members of the rare earth series.

It may be found that e.g. neodymium selenide has a functional optimum over the range $100^\circ\text{--}600^\circ\text{C}$ and that dysprosium selenide produces high outputs from $500^\circ\text{--}1500^\circ\text{C}$; the possibility thereby may exist that $(\text{Nd Dy})_2\text{Se}_3$ will be functional over a very wide range. That the rare earth metals are highly soluble in each other suggests immediately the possible preparation of materials of almost any desired average conduction band width.

APPENDIXOBSERVATIONS ON SOME GADOLINIUM-SELENIUM COMPOUNDS

By: H. M. Muir, V. F. Novy, and R. C. Vickery

Studies are in progress in these laboratories on the thermoelectric and semi-conductor properties of some gadolinium intermetallic compounds and these have necessitated tentative delineation of phase parameters. Presented here is a preliminary report resulting from this work, on that portion of the gadolinium-selenium system between 50 and 70 atomic % selenium, i.e., corresponding to the region of GdSe , Gd_2Se_3 and GdSe_2 intermetallic compound formation.

In recent studies, rare earth-selenium "compounds" have been interpreted from the standpoint of ionic stoichiometry.^{1,2} The semi-conductor nature of some analogous rare earth compounds³ suggests, however, that the selenides are not wholly ionic entities but are probably intermetallic in nature and possess a degree of covalent bonding.

EXPERIMENTAL

The compositions reported here have been prepared by a two state technique. An initial vapor phase reaction is affected between appropriate amounts of gadolinium and selenium in a length of 1/2" OD Vycor tubing. After sealing one end of the tube, gadolinium metal (99.8% purity) is introduced in the form of chips of approximately 1/32" cube size. A constriction is then drawn by melting the tube above the metal chips and, after cooling, selenium metal (99.9% grade) in 1/16" dia. pellets is introduced above the constriction. Direct solid contact of the reactants is thus prevented. After evacuating the system the open end of the tube is sealed off and the whole is inserted into a tube combustion furnace. The furnace temperature is then slowly increased at a rate approximating 100°C per hour up to 900°C. This temperature is maintained for 24 hours and the system then allowed to cool to room temperature at approximately 200°C per hour. Reaction between gadolinium metal and selenium normally becomes explosively exothermic at ca 500°C; by using the gradual heating technique indicated however, sufficient selenium appears to be absorbed by the gadolinium before this point is reached and the reaction then becomes controllable.

From this reaction, the compositions are obtained as powders. These are consolidated by pressing, at 15,000 psi., into pellets approximately 1-1/4" dia. by 1 1/2" thick. From this point treatment involves either sintering in a Kinney F9 high vacuum furnace at 1650 - 1700°C, or arc melting under argon with a non-consumable tungsten electrode against a water-cooled copper hearth.

Using -200 mesh powders of the materials prepared, X-ray diffractograms have been obtained through a GE XRD-5 diffractometer employing nickel-filtered copper radiation. All materials prepared were friable, and annealing, after comminution, for relief of stresses, was found to be necessary.

Resistivity and Seebeck coefficient values have been obtained on samples approximately 1.25 x 0.6 x 0.6 cm. For resistivity determination, the samples are inserted into a Vycor tube and seated firmly against four, externally spring loaded, stainless steel electrodes. The two outer electrodes supply the current from dry cells (100-300 ma range) and measurements are made from the two inner electrodes through a Kintel electronic galvanometer. Accuracy of $\pm 5\%$ is felt to be obtained.^{4,5}

For measurements at elevated temperatures, a non-conductive Kanthal wire heater is used as the heat source and is controlled to $\pm 1^\circ\text{C}$ over the entire heating range through a Wheelco unit. The heating chamber is purged continuously with argon gas and no contact contamination has been observed thus far with temperatures up to 1000°C.

In determination of Seebeck coefficients, the samples are placed with their polished sides between two platinum plate electrodes which are maintained in firm contact with the specimen by pressure from stainless steel rods, externally spring-loaded. The whole unit is contained in a Vycor tube through which argon is passed continuously during the heating and cooling cycle.⁵

An alumina thermocouple sheath containing a chromel/alumel thermocouple is inserted through the center of each stainless steel rod and extended to the platinum electrodes. A separate cold junction is used for each thermocouple employed for measuring the thermal gradient through the sample. The heat source is a nichrome wound wire heater assembled around the Vycor tube.

The platinum electrode assembly appears to be functioning satisfactorily at temperatures up to 1000°C and has shown no evidence of contamination. A switching circuit

is provided to allow the rapid routing of both chromel/alumel thermocouples, as well as Seebeck emf, to a Kintel electronic galvanometer. Again, accuracy of measurements is felt to be $\pm 5\%$.

Magnetic susceptibilities have been determined by using equipment previously described⁶ in which a transducer measures the force exerted on the sample in a magnetic field of known magnitude.

Standard techniques have been used for chemical analysis.⁷

DATA OBTAINED

In addition to the precise physical measurements made, reaction products were examined metallographically. Such studies, allied with preparative data, suggested strongly that Gd_2Se_3 is the most stable composition of that part of the system studied and probably of the whole Gd-Se System. All preparations containing more than 50% selenium after the vapor phase reaction, liberated selenium vapor upon subsequent heating in air, argon, or vacuum, and resolved to the 2:3 composition at temperatures ca 700 - 750°C. The crystal structure assigned to Gd_2Se_3 (below) did not appear in X-ray diffractograms of materials prepared below about 750°C. When once this structure had been established by arc melting or sintering at 1400°C, it persisted at low temperatures and showed no signs of disruption after several thermal cyclings.

A temperature in the range 700 - 750°C appears to be the limit of thermal stability of GdSe_2 . Above these temperatures it too decomposes to yield the 2:3 compound and free selenium vapor. At compositions below the 2:3 ratio only one compound has been observed, that of GdSe . A preparation, slightly on the gadolinium-rich side of Gd_2Se_3 , heated at 1380°C for a short period, exuded a liquid material shown metallographically to be a eutectic. This material contained 60% Gd i.e., the theoretical requirement of Gd_3Se_4 .

GdSe: This compound appears to melt at approximately 1450°C. X-ray diffractometry shows the compound to be isomorphous with the other rare earth monoselenides examined by Klemm and Koczy.⁸ Data obtained indicates the probable structure to be as follows:

B1 (NaCl) structure

Cubic: O_h^5 - F mzm

$a_0 = 5.758\text{\AA}$; X-ray density = 8.2

Unit volume = 190.9A³ Z=4

Each selenium atom is believed to be surrounded by six gadolinium atoms at the vertices of a regular octahedron. From the unit cell size the Gd-Se distance was calculated to be 2.88A and Gd-Gd 5.76A. The cell parameter is smaller than the theoretical distance of 5.92A required for atomic radii of 1.79 for Gd and 1.17 for Se. This contraction is attributed to the development of covalent characteristics and represents a decrease of 4% in the Gd radius, assuming that of Se to remain unaffected.

Separation of the gadolinium atoms by selenium is of such nature that anything except long range Van der Waals forces between them can be discounted.

Gd₂Se₄: No evidence has been found for the separate existence of a compound of this composition. At 1380°C a eutectic is found of the 1:1 and 2:3 compounds which corresponds to this composition. At low temperatures, as will be indicated below, this composition is believed to represent the point at which selenium atoms occupy all interstitial sites in the cubic GdSe. With the introduction of more selenium into the system at low temperatures, the structure then converts and distorts to that of the orthorhombic GdSe₂.

A disordered structure of the GdSe - Se interstitial form would correspond to the Th₃P₄ type, (D_{7h}) T₈ - 143d, in which 10-2/3 gadolinium atoms would randomly occupy the thorium positions. Metallographic and X-ray evidence shows that such a structure cannot be isomorphous with that found for the Gd₂Se₃ compound.

Gd₂Se₃: This compound is apparently the most stable of the system as thus far examined. It melts congruently at ca 1750°C and crystallizes in b.c.c. form with $a_0 = 8.71\text{\AA}$.

In the ordered assembly postulated for this compound, a degree of covalent bonding between Gd-Se atoms is again suggested. The Gd-Gd distance is 4.072A and that of Gd-Se less than the theoretical 2.96A. A tight packing of the selenium atoms, which may assume the selenium spiral, indicates ionic bonding between these atoms.

GdSe₂: Least stable of the compounds found in the region examined, this decomposes above 200°C and gradually loses selenium. If maintained at a temperature of ca 500°C for a prolonged period, resolution to GdSe and Se vapor is complete. If heating is rapid and the temperature is raised rapidly to ca 700 - 750°C, Gd₂Se₃ is formed with Se vapor. The compound may therefore be considered as deriving from interstitial emplacement of selenium in the GdSe lattice. The compound prepared at low temperatures has an orthorhombic type structure with a_0 : 7.27Å b_0 : 4.03Å c_0 : 8.30Å. Isomorphism is believed for this structure with that reported⁹ for ThSe₂ - C23 type (D_{2h}¹⁶ -- pnma) and attempts are now being made to prepare this compound in single crystal form for closer examination.

Electrical Measurements: Resistivity and Seebeck coefficient values obtained through the series and shown in Table 1, confirm indications previously given³ of semiconductor characteristics for rare earth chalcogenides. This, in turn, is suggestive of a degree of covalent bonding in the compounds found. Preliminary measurements of Hall effect confirm this, showing p type conductivity with mobilities of the order previously reported.³

TABLE I
MAGNETIC AND ELECTRICAL PROPERTIES OF GADOLINIUM
SELENIDES

| Compound | $\chi_m \times 10^6$ (c.g.s.) | μ_{eff} | Resistivity (Microhm-cm) | | Seebeck Coefficient ($\mu\text{V}/^\circ\text{C}$) | |
|-------------------------------------|----------------------------------|--------------------|-----------------------------|--------|--|-------|
| | | | 200°C | 600°C | 200°C | 600°C |
| GdSe | 934 | 0.34 | 180 | 233 | 22.0 | 18.0 |
| Gd ₂ Se ₃ (1) | 100 | 0.10 | - | - | - | - |
| (2) | 566 | 0.40 | 37.000 | 48.000 | 278 | 423 |
| (3) | 1310 | 1.70 | 1300 | 43.000 | 350 | 422 |
| GdSe ₂ | 4760 | 0.13 | 6400 | 12.500 | 150 | 205 |

1. Direct vapor reaction product (900°C).
2. Reaction product from (1), sintered (1700°C).
3. Reaction product from (1), arc melted (3000°C).

Magnetic Data: Room temperature susceptibilities, and Bohr magneton numbers obtained by studies at low temperatures, are also shown in Table 1. Where similar compositions have been prepared, good agreement is found with data of previous workers.^{1,3} Of specific interest are the data shown for Gd_2Se_3 at different preparation temperature levels. These would seem to confirm to a mild degree, the assertion of Benaceraff et al¹ that Gd_2Se_3 can exist in two modifications. However, X-ray diffractometry has not discerned such a dual entity and the possibility must be considered that, in the earlier methods of preparation, retention of oxyselenide was a possibility.

Chemical Characteristics: All compositions examined in the Gd-Te system are soluble in dilute hydrochloric acid with evolution of hydrogen selenide. Hydrolysis of all compounds is noted in humid air but lack of agreement is found with previous statements¹ that the selenides carburize below 1700°C. In preparing specimens for examination, some have been melted in graphite crucibles in the vacuum furnace with no evidence of carbide formation. Other workers³ have similarly found graphite to be without effect upon these compounds.

DISCUSSION

Insufficient information is yet considered available to warrant the construction of even a partial phase diagram for this system, but the foregoing observations would seem to permit the following rationalization.

Our data on gadolinium monoselenide appear to agree with those given in referenced work. The relationship between the mono and diselenides appears to develop as follows. The cubic GdSe lattice can accept selenium atoms interstitially forming, in part $GdSe_2$. However, not until a composition equivalent to Gd_3Se_4 is reached, does the cubic lattice become strained to the orthorhombic conformance required for $GdSe_2$. The situation would seem analogous to that existing in the CeO_2 - La_2O_3 system¹⁰ in which CeO_2 is unable to impose its fluorite-type structure upon that of La_2O_3 (A-M $2O_3$ type) until its concentration reaches about 40 mol %. In the gadolinium-selenium system, the proximity of this lattice change point to the Gd_3Se_4 composition may account for previous assumptions of the existence of such a compound having a "lacunary" structure.¹ Again, the existence of a high temperature eutectic at the 3:4 composition is further evidence against the existence of a Gd_3Se_4 entity.

The existence of high and low temperature phases of Gd_2Se_3 has also been suggested. Little confirmatory evidence has however been found for this except for magnetic data; X-ray and metallographic examinations indicate that, in low temperature preparations, compositions equivalent to Gd_2Se_3 are composed of GdSe with GdSe_2 or Se .

The Th_3P_4 structure assigned by Benacerraf et al (loc. cit) to Gd_2Se_3 is difficult to accept since X-ray scans on monophase materials show intensity maxima prohibited by that structure. It must be remembered, however, that modes of preparation have differed and interstitial hydrogen or oxygen absorption might effect some degree of disorder in the Th_3P_4 type structure. Again, because attempts by Benacerraf et al, to prepare GdSe_2 were carried out at 450°C and upwards, loss of selenium to give compositions approximating Gd_2Se_3 is understandable because of the temperature instability of the biselenide.

Magnetic data and the results of electrical measurements would seem to indicate a degree of covalent bonding in the compounds formed. It is suggested that this might involve hybridization of $\text{Gd } 5d, 6s$, and $\text{Se } 4p$ electrons. Some justification is seen for this in the high temperature stability of the "balanced" 2:3 compound and the tendency of compositions on either side of it to lose less strongly held gadolinium and selenium on heating.

The resistivity of GdSe finds a counterpart in that of ErSe^3 which has been interpreted by Iandelli¹¹ as indicating the existence of only one conduction electron in compounds of this form. The higher resistivities found for Gd_2Se_3 and GdSe_2 would suggest a tendency in these compounds towards ionic characteristics, but the magnetic moments found do not confirm a purely ionic nature. Again, the high thermal stability of Gd_2Se_3 , combined with the foregoing considerations, may be interpreted, with Welker¹², in terms of resonance between the covalent and ionic contributions to the bond.

Acknowledgements are made of the assistance of E. Avis and W. C. Sexton in making electrical and magnetic measurements on the materials prepared and of Dr. S. Samson for advice in interpretation of X-ray data.

REFERENCES

1. Benacerraf, A. et al: Comptes. rend. 248 1672, 2012 1959.
2. Menkov, A. A. et al: Doklady Akad Nauk. S.S.S.R. 128 92, 1959.
3. Miller, G. F. et al: J Electrochem. Soc. 106 1043 1959.
4. Valdes, L. B.: Proc I.R.E. 42 420 1954.
5. Avis, E. and Vickery, R. C.: J. Appl. Physics (in the press).
6. Vickery, R. C. and Sexton, W. C.: Rev. Sci. Instr. (in the press).
7. Vickery, R. C.: "Analytical Chemistry of the Rare Earths": Pergamon N. Y. 1960.
8. Klemm, W. and Koczy, A.: Z. Anorg. Allgem. Chem 84 233 1937.
9. D'eye, R. W. M. et al: J. Chem. Soc. (London) 1952 2555 1953 1760.
10. Brauer, G. and Haag, H : Z. Anorg. Chem. 266 345 1951.
11. Iandelli A.: Gazzeta Chem. 85 881 1955.
12. Welker, G.: Physica. 20 893 1954.

TABLE I
GADOLINIUM-ANTIMONY SYSTEM,
PHYSICAL DATA

| <u>NOMINAL COMPOSITION (Arc Melted)</u> | <u>(Sb %) NOMINAL</u> | <u>(Sb %) ACTUAL</u> | <u>MELTING POINT</u> |
|---|----------------------------|---------------------------|----------------------|
| Gd ₃ Sb | 20.4% | 16.0% | 1170°C |
| Gd ₂ Sb | 28.0% | 26.7% | 1700°C |
| Gd ₃ Sb ₂ | 33.7% | 29.3% | 1830°C |
| GdSb | 43.7% | 37.4% | 1920°C |
| GdSb ₂ | 60.8% | 48.3% | 1820°C |
| Gd ₃ +Sb ₂ * | 30.7% | 33.0% | 1515°C |
| Gd ₃ Sb ₂ ** | 36.7% | 27.5% | 1800°C |

* Gd₃+Sb₂ plus 3.0% excess gadolinium

** Gd₃Sb₂+ plus 3.0% excess antimony

TABLE II
GADOLINIUM-ANTIMONY SYSTEM,
ELECTRICAL DATA

| NOMINAL COMPOSITION (Arc Melted) | RESISTIVITY (microhm-cm) | | | SEEBECK COEFFICIENT ($\mu\text{V}/^\circ\text{C}$) | | |
|--|--------------------------|---------------------|---------------------|--|---------------------|---------------------|
| | 30°C | 200°C | 600°C | 30°C | 300°C | 600°C |
| Gd_3Sb | 230 | 250 | 287 | 13 | 26 | 25 |
| Gd_2Sb | 140 | 270 | 348 | 25 | 25 | 25 |
| Gd_3Sb_2 | 288 | | | 31 | 31 | 29 |
| GdSb | 147 | | | 21 | 21 | 16 |
| GdSb_2 | 180 | 199 | 293 | 16 | 21 | 20 |
| Gd_3Sb_2 | 237 | | | 25 | 25 | 26 |
| $\text{Gd}_3\text{Sb}_2 +$ | 191 | 220 | | 34 | 32 | 29 |
| | | | | | | 27 |

TABLE III
GADOLINIUM-BISMUTH SYSTEM,
PHYSICAL DATA

| <u>NOMINAL COMPOSITION (Arc Melted)</u> | <u>(Gd %) NOMINAL</u> | <u>(Gd %) ACTUAL</u> | <u>MELTING POINT</u> |
|---|---------------------------|--------------------------|----------------------|
| Gd ₃ Bi | 69.3% | 70.3% | 1180°C |
| Gd ₄ Bi ₃ | 50.0% | 51.8% | 1600°C |
| GdBi | 42.6% | 42.8% | 1670°C |
| GdBi ₂ | 27.3% | 27.5% | 1620°C |
| Gd ₄ Bi ₃ * | 53.0% | 52.0% | 1600°C |
| Gd ₄ Bi ₃ † ** | 47.5% | 48.0% | 1680°C |

* Gd₄Bi₃ plus 3% gadolinium

** Gd₄Bi₃† plus 3% bismuth

TABLE IV
GADOLINIUM-BISMUTH SYSTEM,
ELECTRICAL DATA

| NOMINAL COMPOSITION (Arc Melted) | RESISTIVITY (microhm-cm) | | | SEEBECK COEFFICIENT | | $(\mu\text{V}/^\circ\text{C})$ 80°C |
|--|--------------------------|---------------------|---------------------|---------------------|---------------------|--|
| | 30°C | 200°C | 500°C | 300°C | 600°C | |
| Gd ₃ Bi | 222 | 232 | 259 | 26 | 29 | 24 |
| Gd ₄ Bi ₃ | 298 | 910 | | 26 | 24 | 27 |
| GdBi | 396 | 470 | | 26.4 | 25 | 28 |
| GdBi ₂ | 109 | 145 | 303 | 13 | 15.2 | 31.8 |
| Gd ₄ +Bi ₃ | 480 | 450 | 465 | 29 | 27 | 27 |
| Gd ₄ Bi ₃ + | 160 | 186 | 241 | 30 | 29 | 27 |

TABLE V
GADOLINIUM-SELENIUM SYSTEM,
COMPOSITIONAL DATA

| COMPOSITION | NOMINAL | | ACTUAL | | COPPER |
|------------------|---------|------|--------|-------|--------|
| | Gd% | Se% | Gd% | Se% | |
| A (Gd_4Se_3) | 56.8 | 43.2 | 56.3 | 43.7 | N.D. |
| B | | | 59.6 | 40.4 | N.D. |
| C | | | 55.4 | 43.28 | 1.32 |
| D | | | 54.9 | 44.91 | .19 |
| E | | | 54.6 | 45.17 | .23 |
| F | | | 55.7 | 42.7 | .60 |
| G | | | 55.2 | 43.5 | .30 |
| H | | | 53.8 | 41.14 | .06 |
| I | | | 56.2 | 41.52 | 2.22 |
| J | | | 56.3 | 42.6 | 1.1 |
| K | | | 57.3 | 42.27 | 0.43 |
| L | | | 57.3 | 42.2 | 0.50 |
| M | | | 57.6 | 41.65 | 0.55 |
| N | | | 57.7 | 41.93 | 0.37 |
| O | | | 57.7 | 41.93 | 0.37 |
| P | 56.8 | 43.2 | 56.7 | 42.93 | 0.37 |
| Q (Gd_3Se_4) | 59.9 | 40.1 | 58.9 | 41.7 | |
| R ($GdSe$) | 66.6 | 33.4 | 67.6 | 32.4 | |

TABLE VI
GADOLINIUM-SELENIUM SYSTEM,
SEEBECK COEFFICIENT DATA

| COMPOSITION | SEEBECK COEFFICIENT ($\mu\text{V}/^\circ\text{C}$) | | | | |
|--------------------------------|--|-------|-------|-------|-------|
| | 100°C | 200°C | 400°C | 600°C | 800°C |
| A | 4 | 17 | 203 | | 394 |
| B | 12 | | 23 | 240 | 202 |
| C | 685 | 580 | 660 | 608 | |
| D | 133 | 160 | 176 | 203 | 213 |
| E | | 130 | 160 | 185 | 155 |
| F | | 130 | 230 | 206 | 208 |
| G | 137 | 179 | 278 | | 306 |
| H | 66 | 63 | 81 | 81 | 53 |
| I | 113 | 166 | 232 | 200 | 202 |
| J | 500 | 480 | 450 | 380 | 350 |
| K | 25 | 22 | 19 | 19 | 19 |
| L | 268 | 413 | 375 | 385 | 385 |
| M | | 75 | 85 | 105 | 125 |
| N | 105 | 130 | 153 | 167 | 167 |
| O | 114 | 127 | 166 | 196 | 176 |
| P | 300 | 350 | | 420 | |
| Q (Gd_3Se_4) | 40 | 40 | | 48 | |
| R | 28 | 21 | | 17 | |

TABLE VII
GADOLINIUM-SELENIUM SYSTEM
RESISTIVITY DATA

| COMPOSITION | <u>30°C</u> | RESISTIVITY (10^{-3} ohm-cm) | | | |
|--------------------------------------|-------------|---------------------------------|--------------|--------------|--------------|
| | | <u>100°C</u> | <u>200°C</u> | <u>400°C</u> | <u>800°C</u> |
| A (Gd ₂ Se ₃) | 15 | | | | |
| D | 210 | | | | |
| F | 300 | | | | |
| G | 335 | | | | |
| I | 31 | | | | |
| J | 1050 | 1050 | 1050 | 1050 | 600 |
| K | 46 | 46 | 46 | 56 | 80 |
| L | 58 | 61 | 72 | 104 | 300 |
| M | 1 | 1.2 | 1.3 | 2.0 | 50 |
| N | 38 | 40 | 46 | 63 | 60 |
| P | | | 58 | 67 | 50 |
| R (GdSe) | .20 | .21 | .21 | .22 | .27 |
| | | | | | .22 |

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TABLE VIII
GADOLINIUM-SILICON SYSTEM
PHYSICAL DATA

| NOMINAL COMPOSITION (Arc Melted) | PERCENT Si | | MELTING POINT |
|--|------------|--------|---------------|
| | NOMINAL | ACTUAL | |
| Gd_3Si | 5.6% | 3.99% | 1820°C |
| Gd_2Si | 8.3% | 8.14% | 1800°C |
| Gd_4Si_3 | 11.8% | 11.2% | 1700°C |
| $GdSi$ | 15.2% | 16.5% | 1620°C |
| $GdSi_2$ | 26.4% | 26.5% | 1480°C |

TABLE IX
GADOLINIUM-SILICON SYSTEM
ELECTRICAL DATA

| NOMINAL COMPOSITION (Arc Melted) | RESISTIVITY (microhm-cm) | | | SEEBECK COEFFICIENT | | | (μV/°C) |
|--|--------------------------|-------|---|---------------------|---|----------------------------|---------|
| | 30°C | 200°C | $\frac{500^\circ\text{C}}{800^\circ\text{C}}$ | 30°C | $\frac{300^\circ\text{C}}{600^\circ\text{C}}$ | $\frac{800^\circ\text{C}}$ | |
| Gd ₃ Si | 294 | 316 | 384 | 30 | 25 | 29 | 23 |
| Gd ₂ Si | 289 | 303 | 385 | | 31 | 27 | 26 |
| Gd ₄ Si ₃ | 560 | 920 | | 20 | 20 | | |
| GdSi | 308 | 400 | | 20 | 21 | 21 | 20 |
| GdSi ₂ | 186 | 214 | 270 | 23 | 25 | 26 | 25 |
| | | | 371 | | | | |

TABLE X
GADOLINIUM-PHOSPHORUS SYSTEM,
ELECTRICAL DATA

| MATERIAL | % PHOSPHORUS ACTUAL | SEEBECK COEFFICIENT ($\mu\text{V}/^\circ\text{C}$) | | | RESISTIVITY ($\mu\text{ohm-cm}$) | | |
|----------|------------------------|--|-------|-------|------------------------------------|-------|-------------|
| | | 30°C | 200°C | 600°C | 30°C | 200°C | 600°C 800°C |
| GdP (1) | 3.79 | | 29 | 27 | 216 | 236 | 302 363 |
| GdP (2) | 5.5 | 21 | 21 | 24 | 133 | 137 | 165 199 |
| GdP (3) | 10.8 (4.0Zn) | | 24 | 22 | 293 | 335 | 489 545 |
| GdP (4) | 11.7 (.4Zn) | | 23 | 25 | 199 | 224 | 299 349 |
| GdP (5) | 12.5 (.06Zn) | 11 | 20 | 29 | | | |
| GdP (6) | 8.44 (.16Zn) | 25 | 22 | 23 | | | |
| GdP (7) | 9.33(19.6Ca) | -2 | -5 | -21 | 3300 | 4200 | 6700 9200 |

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TABLE XI
GADOLINIUM-BORON SYSTEM,
PHYSICAL DATA

| NOMINAL COMPOSITION (Arc Melted) | PERCENT B | | MELTING POINT |
|--|-----------|--------|---------------|
| | NOMINAL | ACTUAL | |
| GdB ₄ | 21.5 | 18.2 | 2000°C |
| GdB ₆ | 28.6 | 26.7 | 2150°C |

TABLE XII
GADOLINIUM-BORON SYSTEM,
ELECTRICAL DATA

| NOMINAL COMPOSITION (Arc Melted) | RESISTIVITY (microhm-cm) | | | SEEBECK COEFFICIENT ($\mu\text{V}/^\circ\text{C}$) | | |
|--|--------------------------|-------|-------|--|-------|-------|
| | 30°C | 300°C | 600°C | 30°C | 300°C | 600°C |
| GdB ₄ | 81 | 110 | 152 | 170 | 26 | 21 |
| GdB ₆ | 30 | 59 | 149 | 213 | 23 | 23 |
| | | | | | | 25 |

TABLE XIII
HAFNIUM-SILICON SYSTEM,
PHYSICAL DATA

| NOMINAL COMPOSITION (Arc. Melted) | PERCENT Si | | MELTING POINT |
|---|------------|--------|---------------|
| | NOMINAL | ACTUAL | |
| Hf ₂ Si | 7.3 | 5.75 | 3000°C |
| Hf ₅ Si ₃ | 8.65 | 8.94 | 2440°C |
| Hf ₄ Si ₃ | 10.55 | 10.7 | 2420°C |
| Hf ₆ Si ₅ | 11.6 | 12.0 | 2190°C |
| HfSi ₂ | 24.0 | 24.9 | 1800°C |

TABLE XIV
HAFNIUM-SILICON SYSTEM,
ELECTRICAL DATA

| NOMINAL COMPOSITION (Arc Melted) | RESISTIVITY (microhm-cm) | | SEEBECK COEFFICIENT ($\mu\text{V}/^{\circ}\text{C}$) | | |
|--|--------------------------|-------|--|-------|-------|
| | 30°C | 300°C | 300°C | 200°C | 600°C |
| Hf ₂ Si | 93 | 131 | 182 | 203 | 35 |
| Hf ₅ Si ₁₃ | | | | | 21 |
| Hf ₄ Si ₁₃ | | | | | 13 |
| Hf ₆ Si ₁₅ | 82 | 111 | 146 | 176 | 22 |
| HfSi ₁₂ | 62 | 81 | 114 | 136 | 18 |
| | | | | | 30 |
| | | | | | 33 |
| | | | | | 17 |
| | | | | | 17 |
| | | | | | 15 |
| | | | | | 16 |
| | | | | | 33 |

TABLE XV
HAFNIUM-BORON SYSTEM
PHYSICAL AND ELECTRICAL DATA

| NOMINAL COMPOSITION (Arc Melted) | PERCENT B | | MELTING POINT |
|--|-----------|--------|---------------|
| | NOMINAL | ACTUAL | |
| HfB | 5.4 | 5.5 | 2020°C |
| HfB ₂ | 10.2 | 10.1 | 3000°C |

| MATERIAL | RESISTIVITY (microhm-cm) | | | SEEBECK COEFFICIENT ($\mu\text{V}/^\circ\text{C}$) | | |
|--------------------------------|--------------------------|-------|-------|--|-------|-------|
| | 300°C | 300°C | 800°C | 300°C | 600°C | 800°C |
| HfB (arc melted) | 33 | 42 | 75 | 19 | 19 | 17 |
| HfB (levitation melted) | | | | 20 | 19 | 20 |
| HfB (hot pressed) | | | | 19 | 20 | 21 |
| HfB ₂ (arc melted) | | | | 19 | 19 | 19 |
| HfB ₂ (hot pressed) | | | | 23 | 20 | 27 |

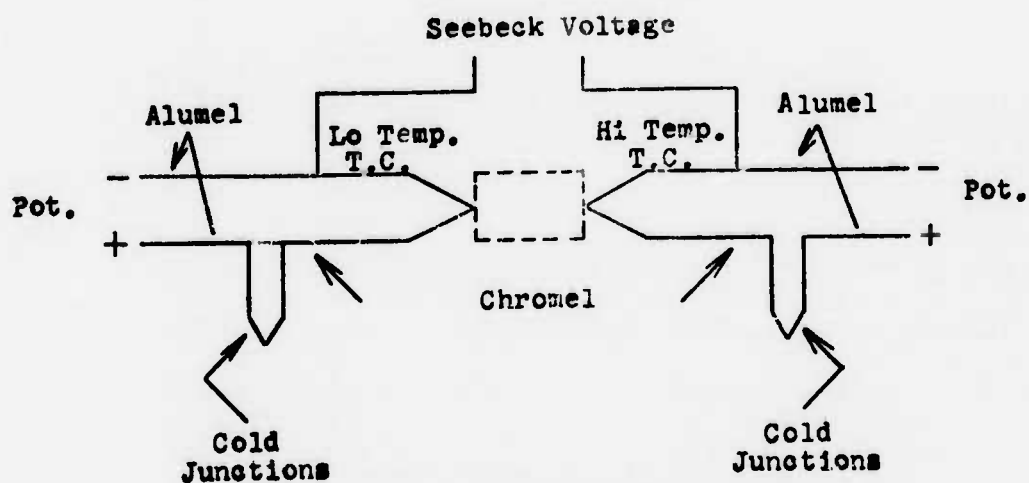
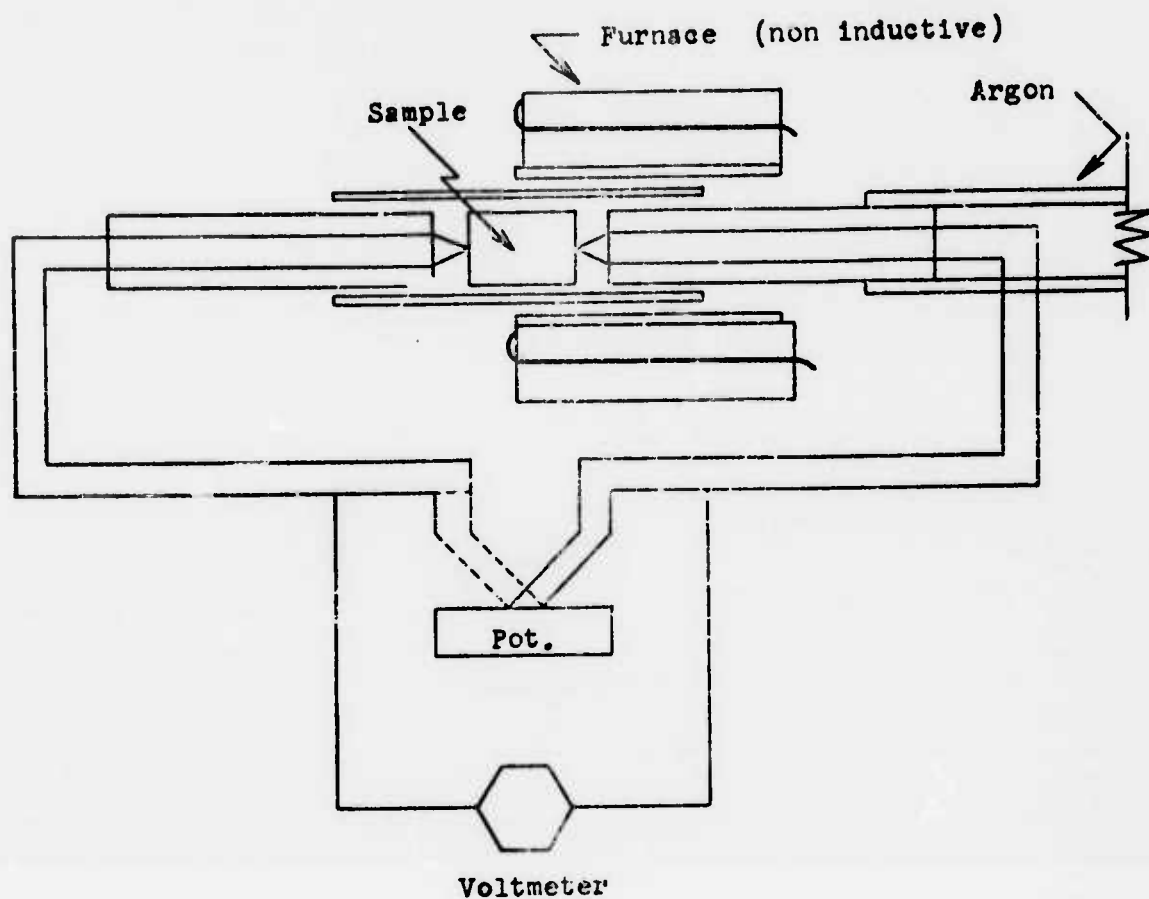
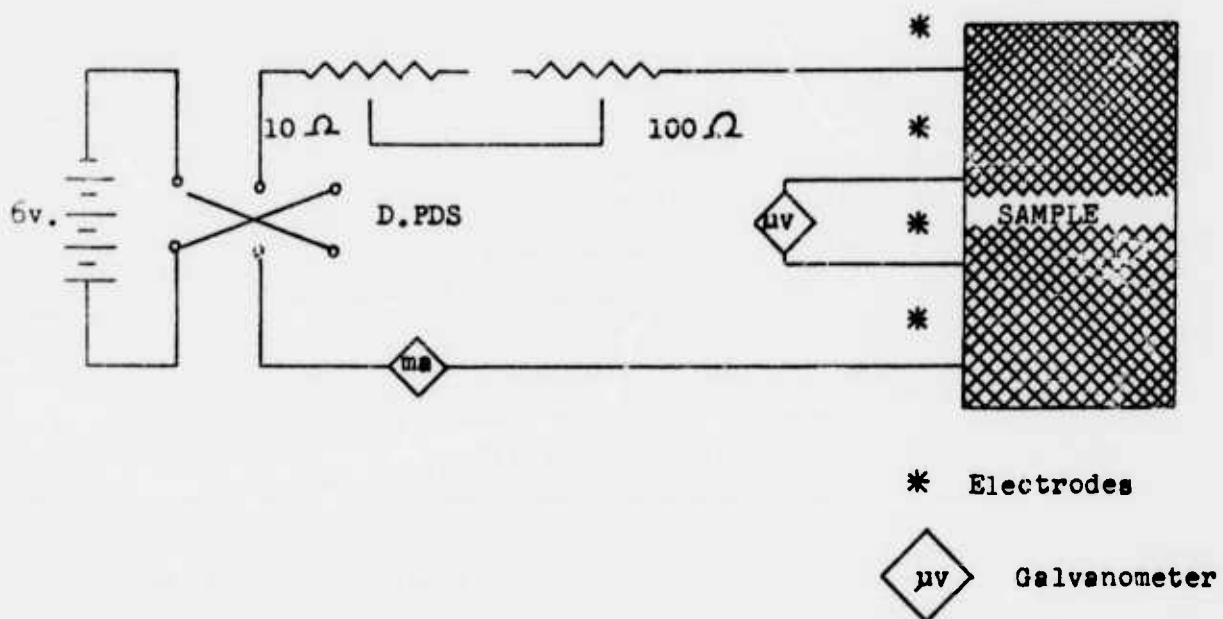


Figure 1 Seebeck Coefficient Apparatus and Circuit

Resistivity Circuit



Resistivity Apparatus

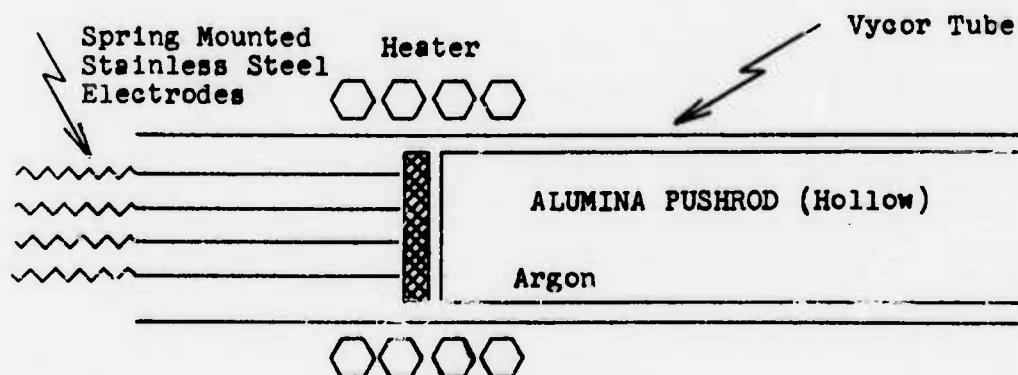


Figure 2 Resistivity Circuit and Apparatus

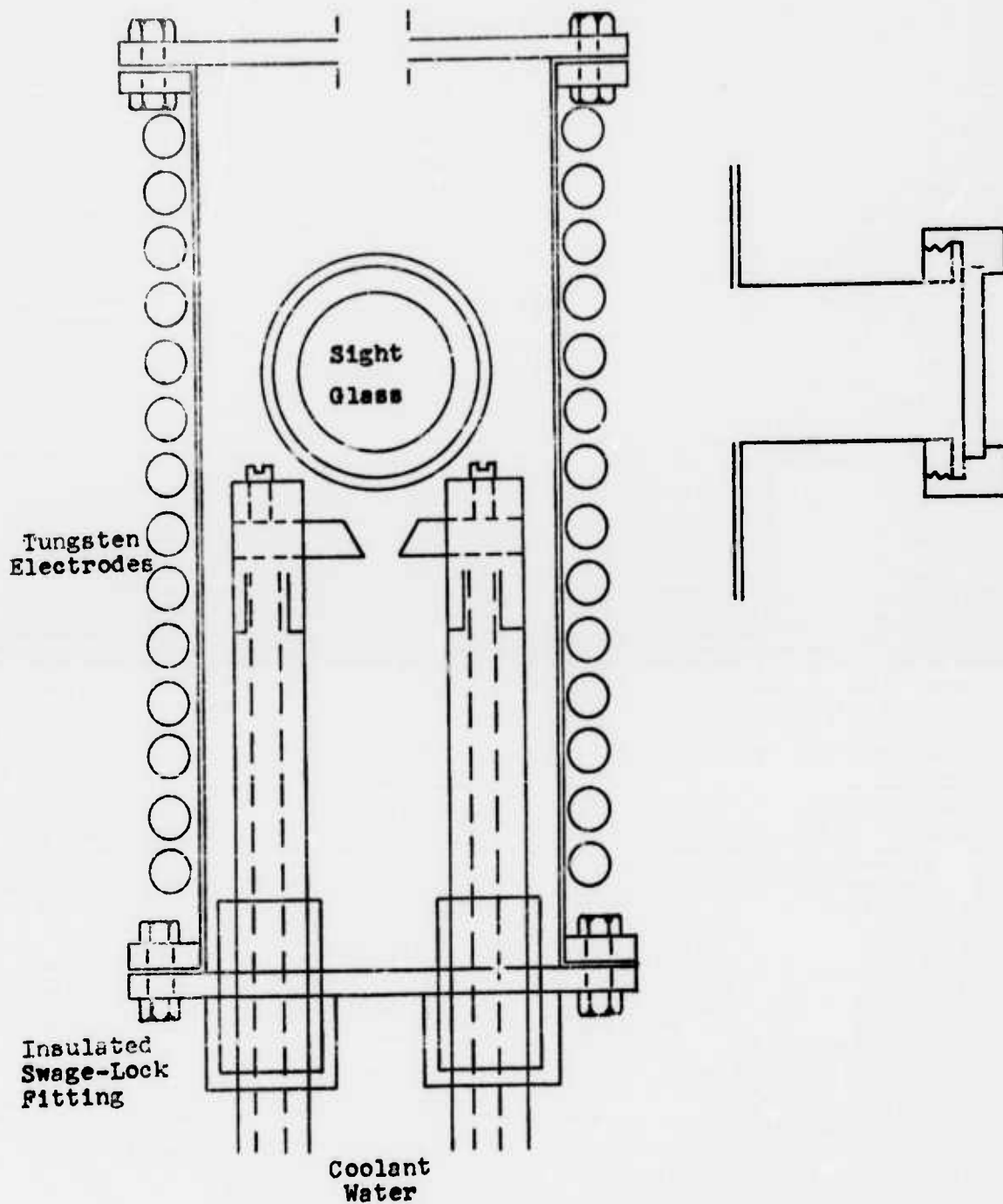


Figure 3 Melting Point Apparatus

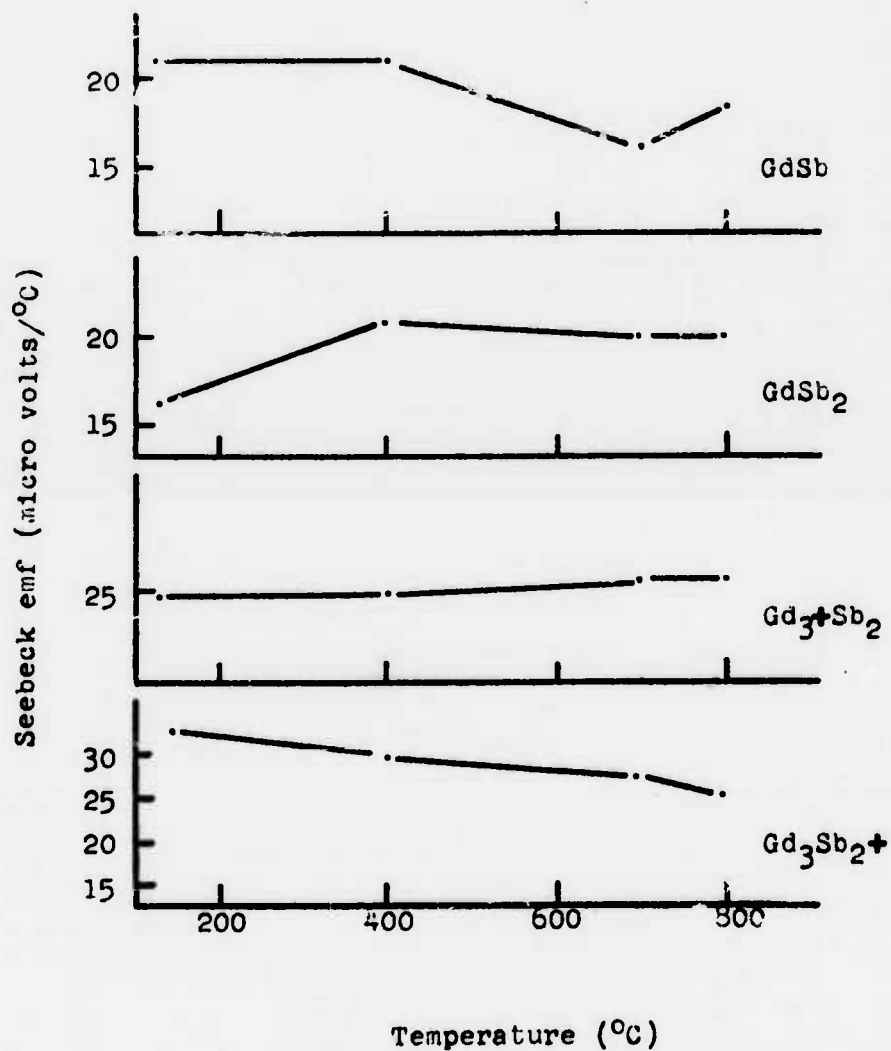


Figure 4 Gadolinium- Antimony System
Seebeck Coefficient vs Temperature

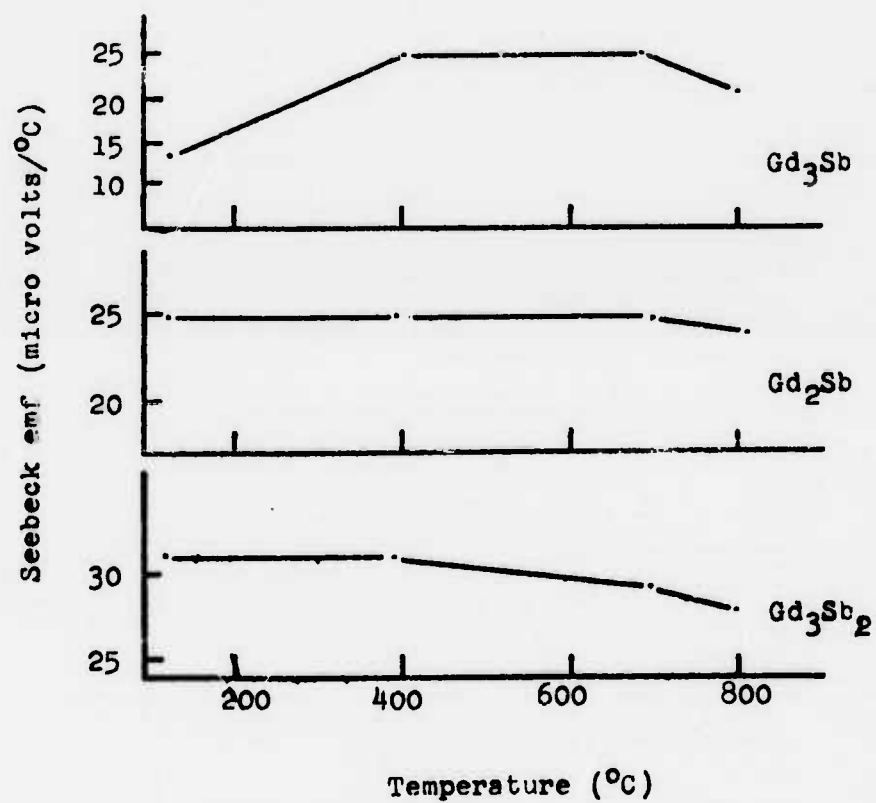


Figure 4 (Continued)

Gadolinium-Antimony System
Seebeck Coefficient vs Temperature

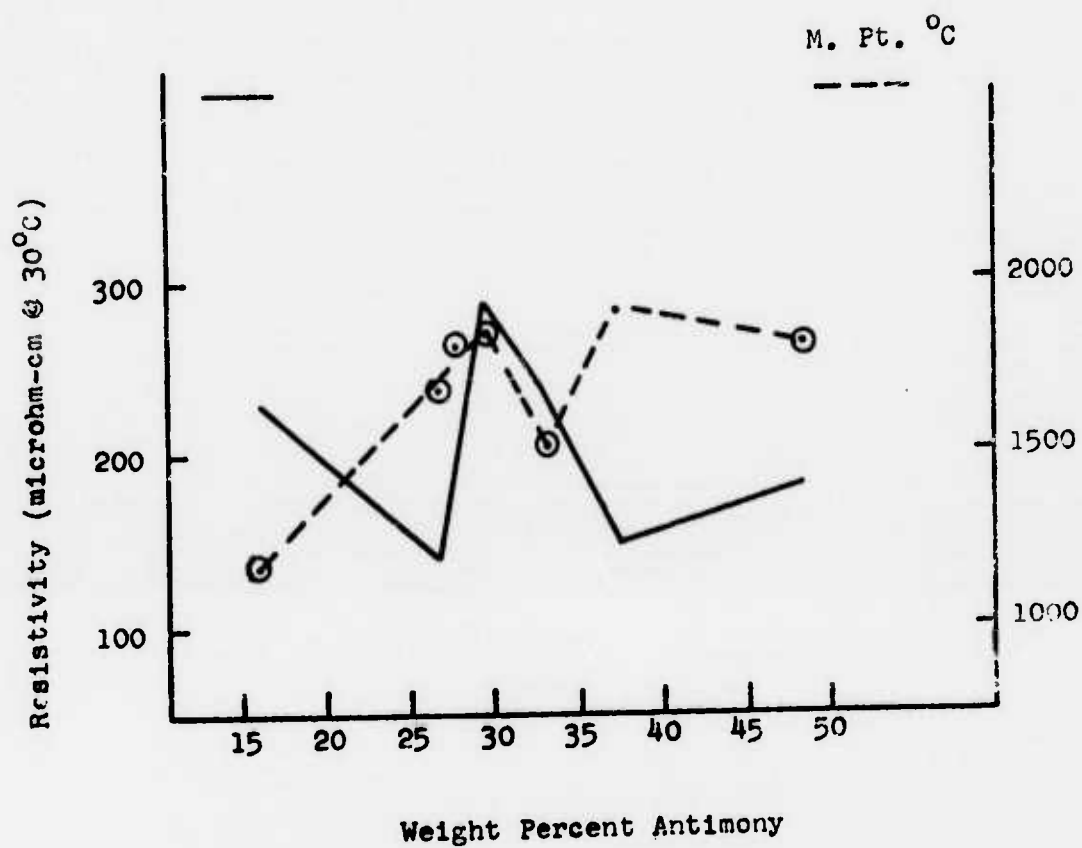


Figure 5 Gadolinium-Antimony System
Resistivity and Melting Points

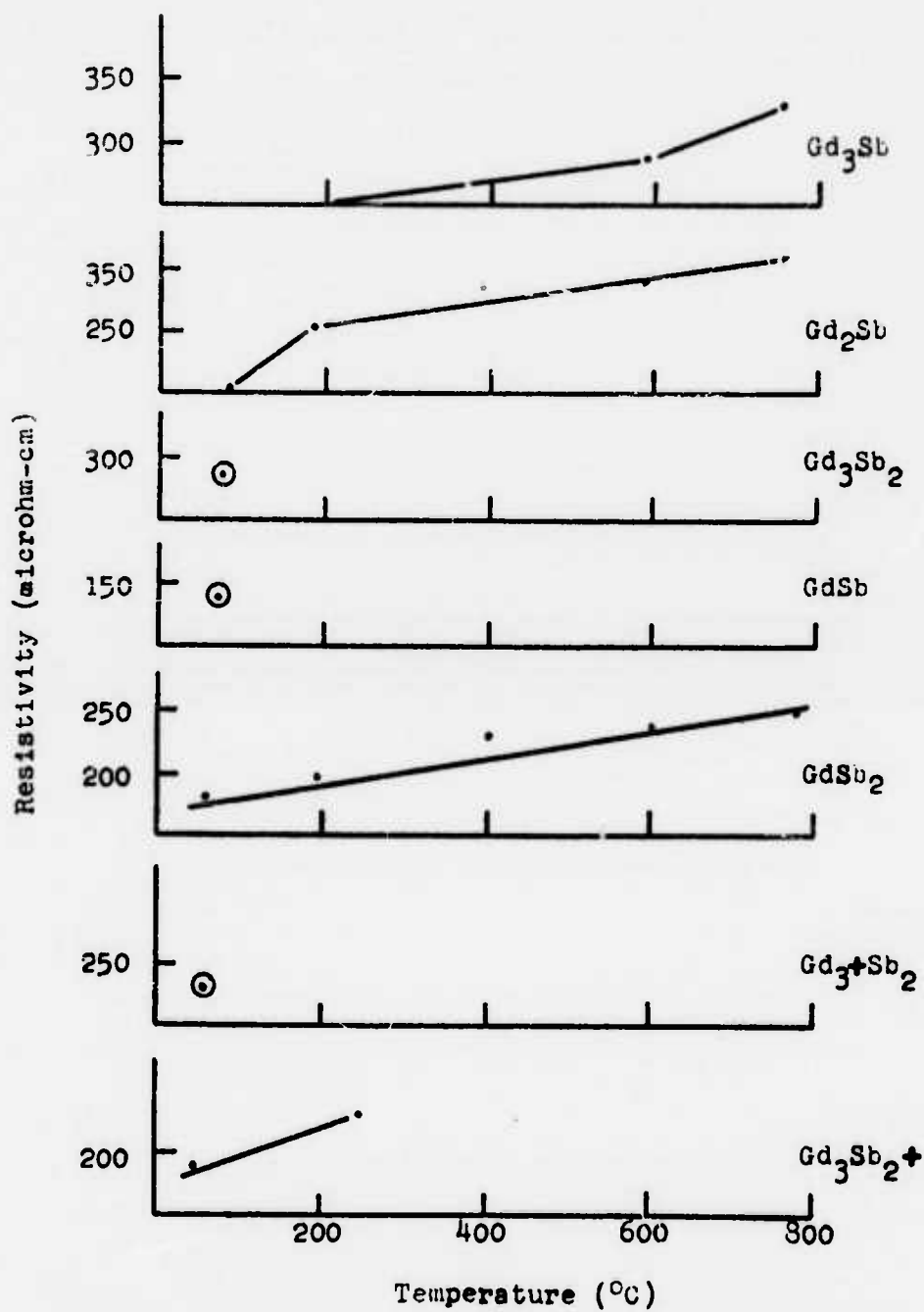


Figure 6 Gadolinium-Antimony System
Resistivity vs Temperature
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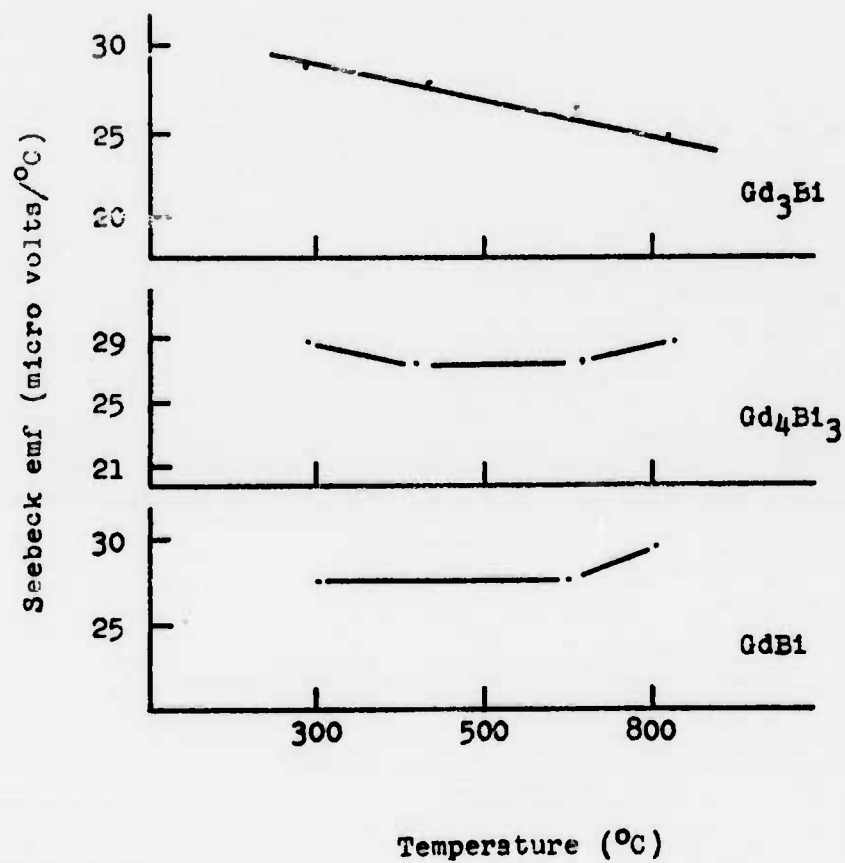


Figure 7 Gadolinium-Bismuth System
Seebeck Coefficients
vs Temperature

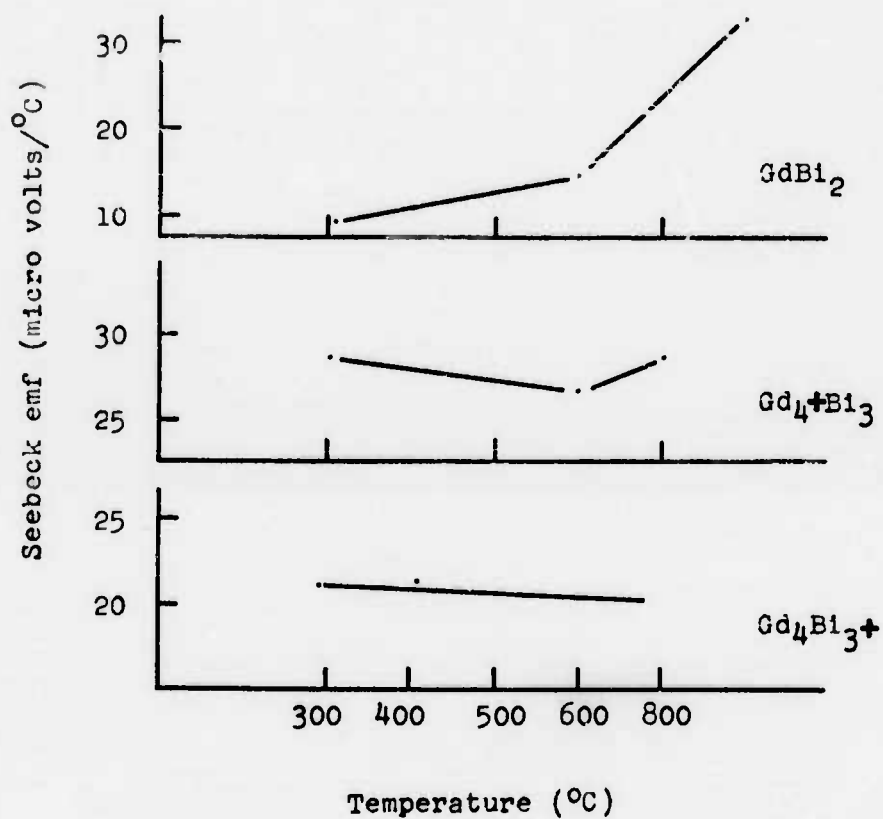


Figure 7 (Continued)

Gadolinium-Bismuth System
Seebeck Coefficients
vs Temperature

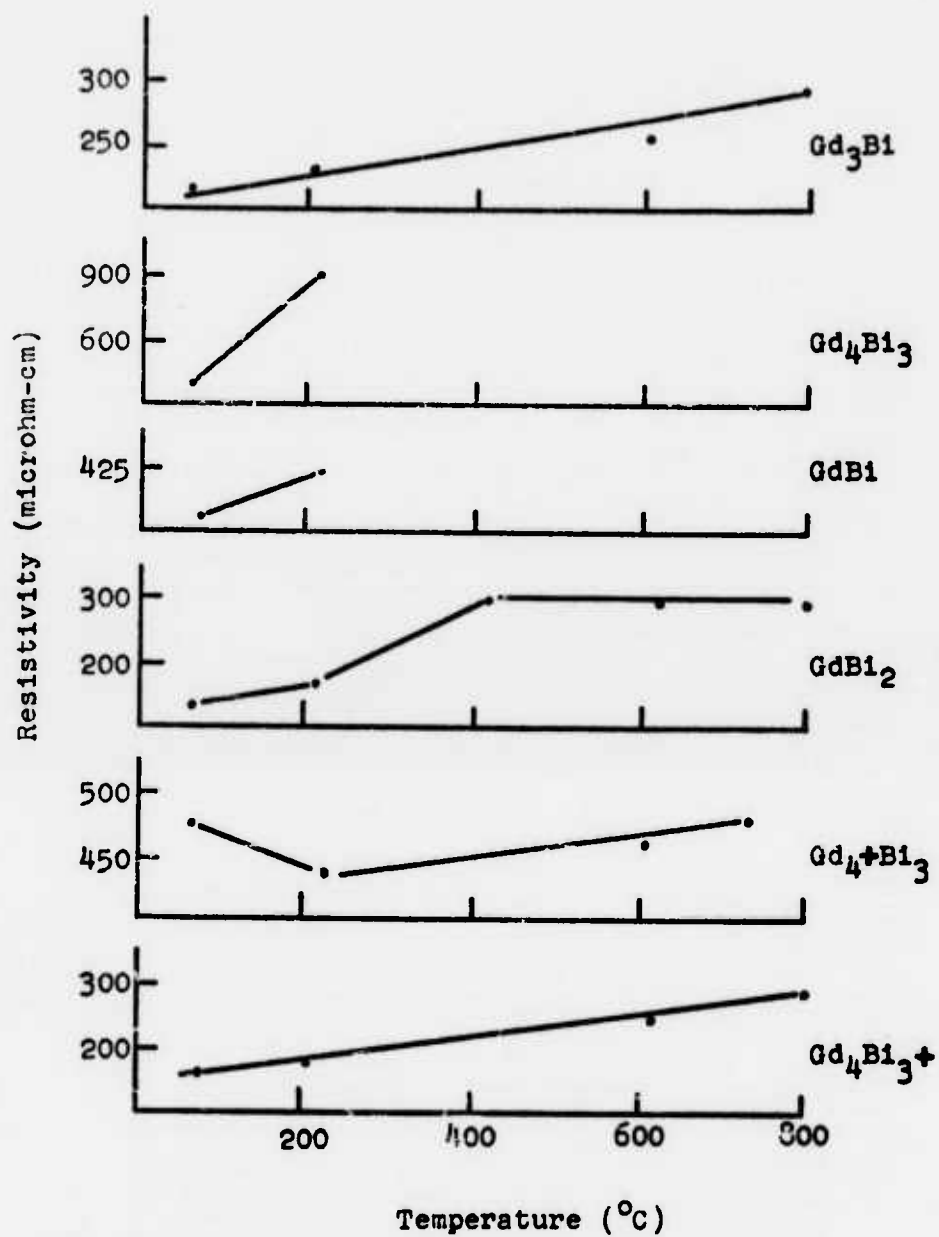


Figure 8 Gadolinium-Bismuth System
Resistivity vs Temperature

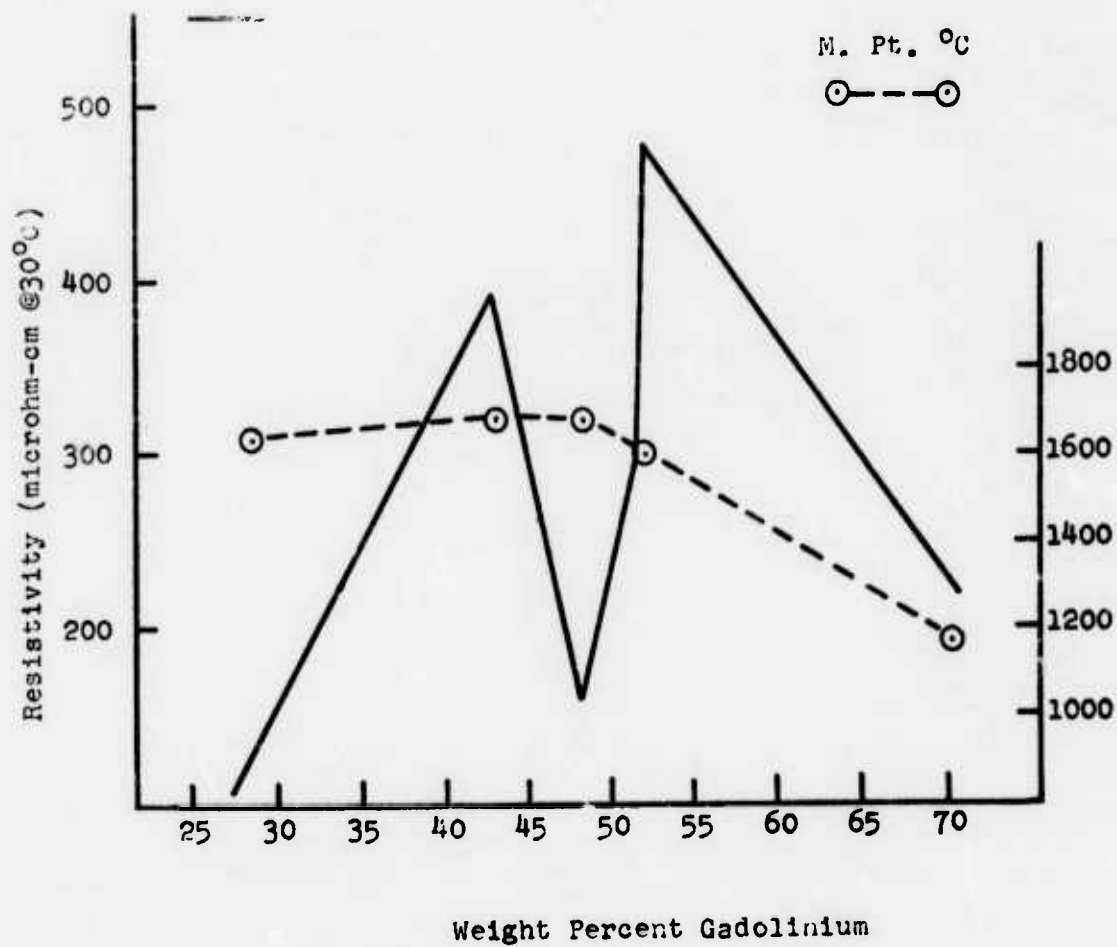


Figure 9 Gadolinium-Bismuth System
Resistivity and Melting Points

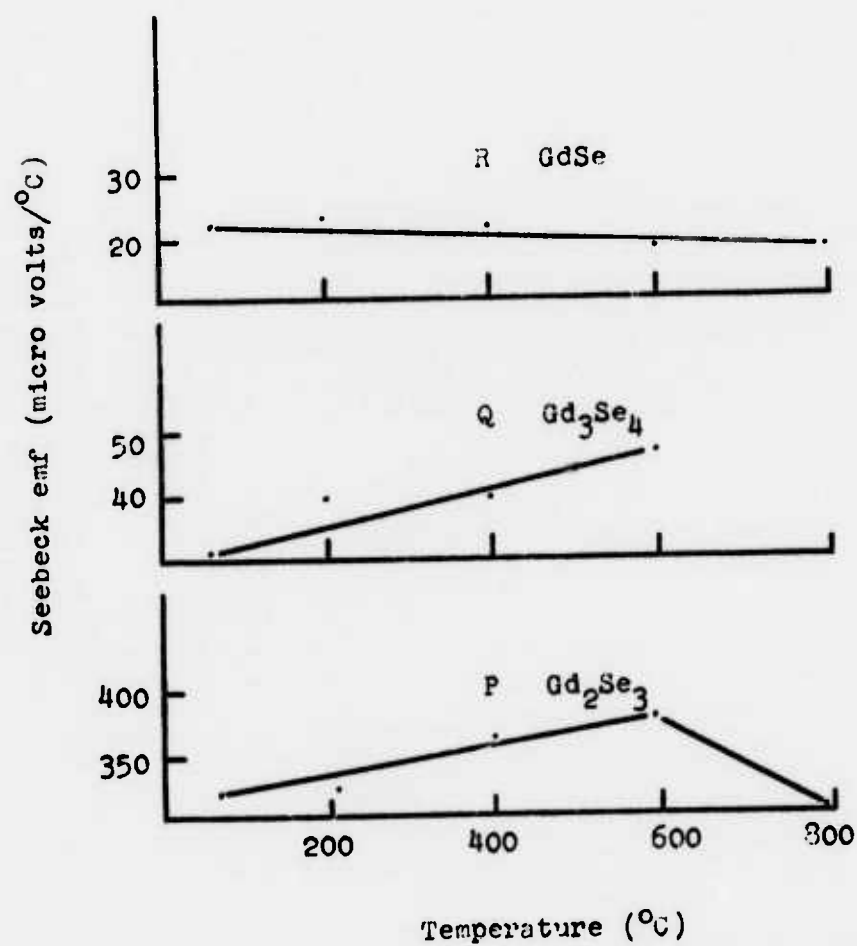


Figure 10 Gadolinium-Selenium System
Seebeck Coefficient vs
Temperature

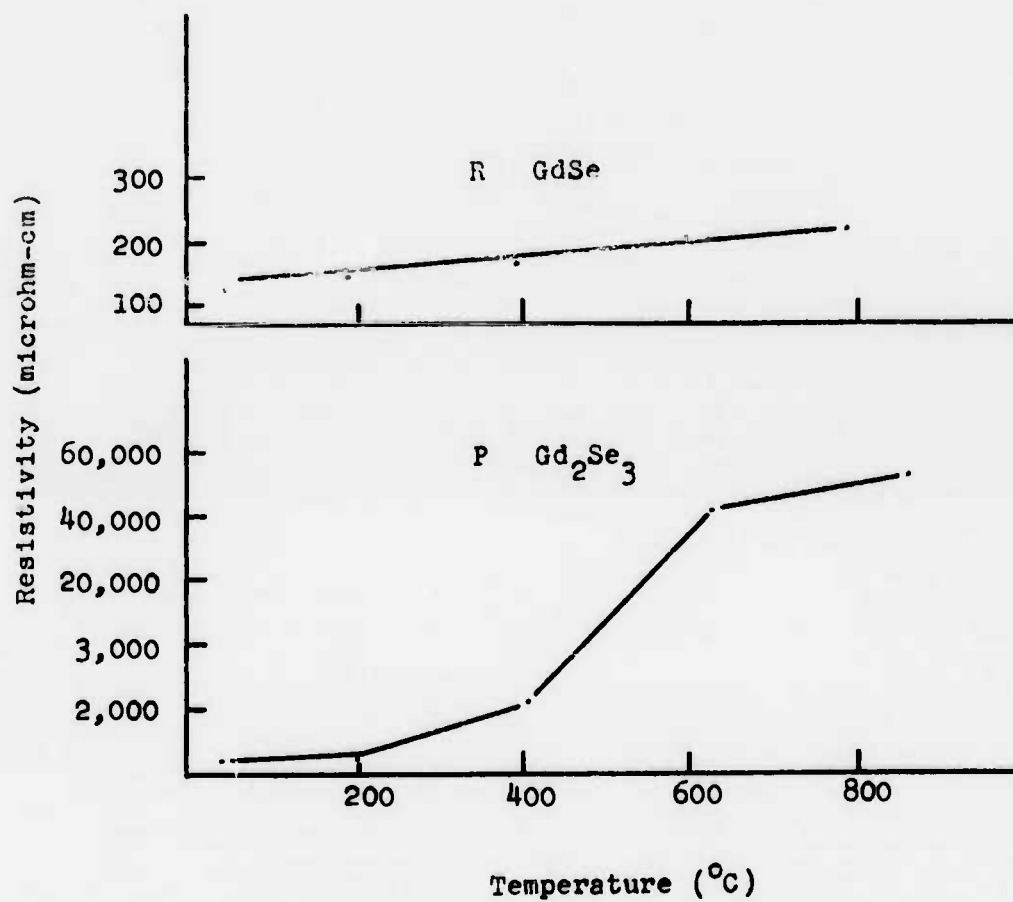


Figure 11 Gadolinium-Selenium System
Resistivity vs Temperature

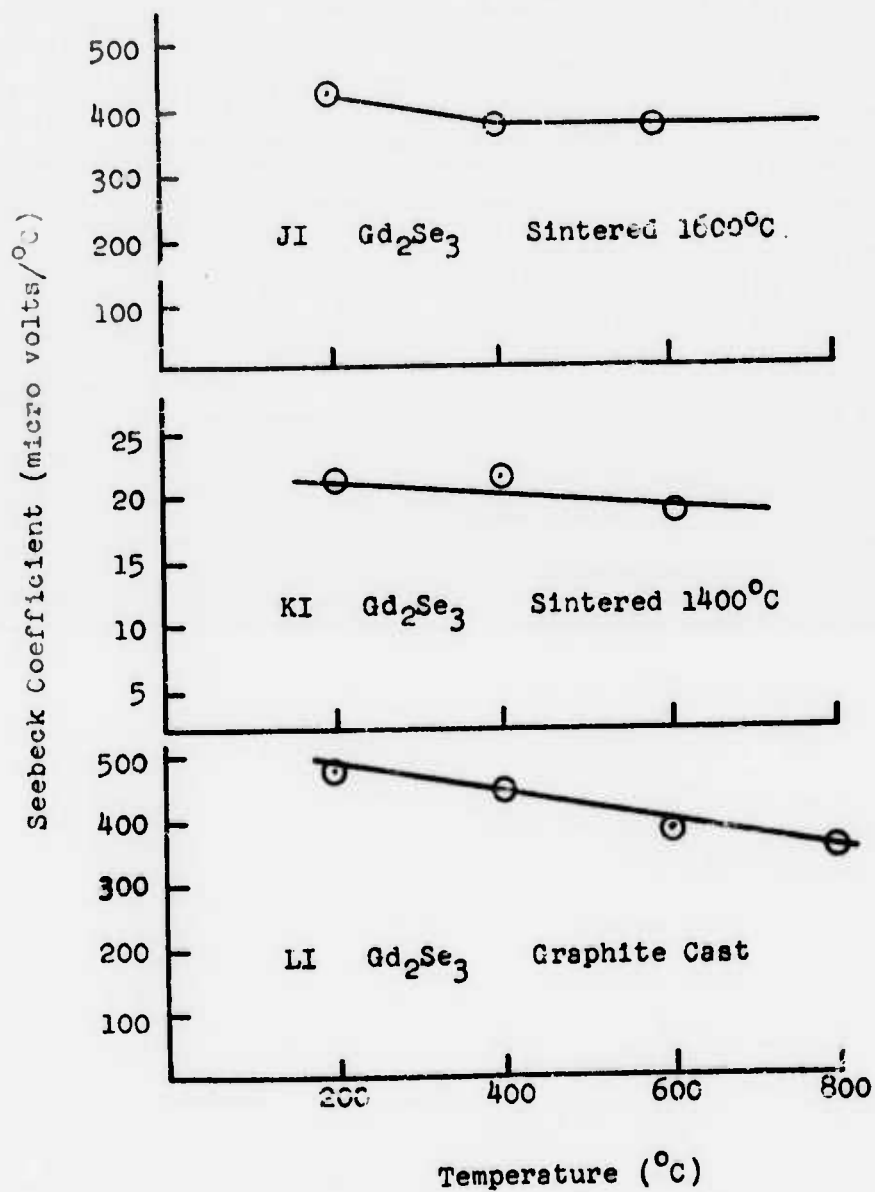


Figure 12 Effect of Processing Variables
Upon Seebeck Coefficient of Gd_2Se_3

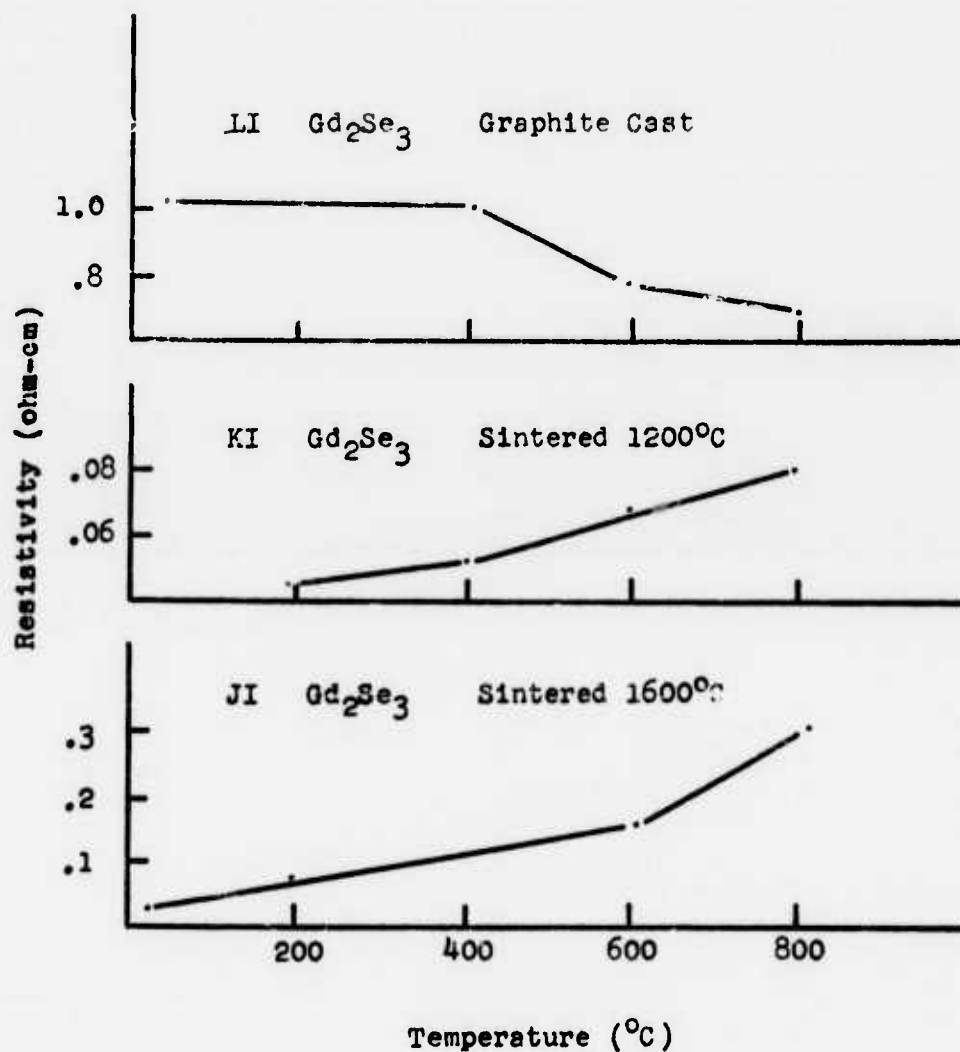


Figure 13 Effect of Processing Variables
Upon Resistivity of Gd_2Se_3

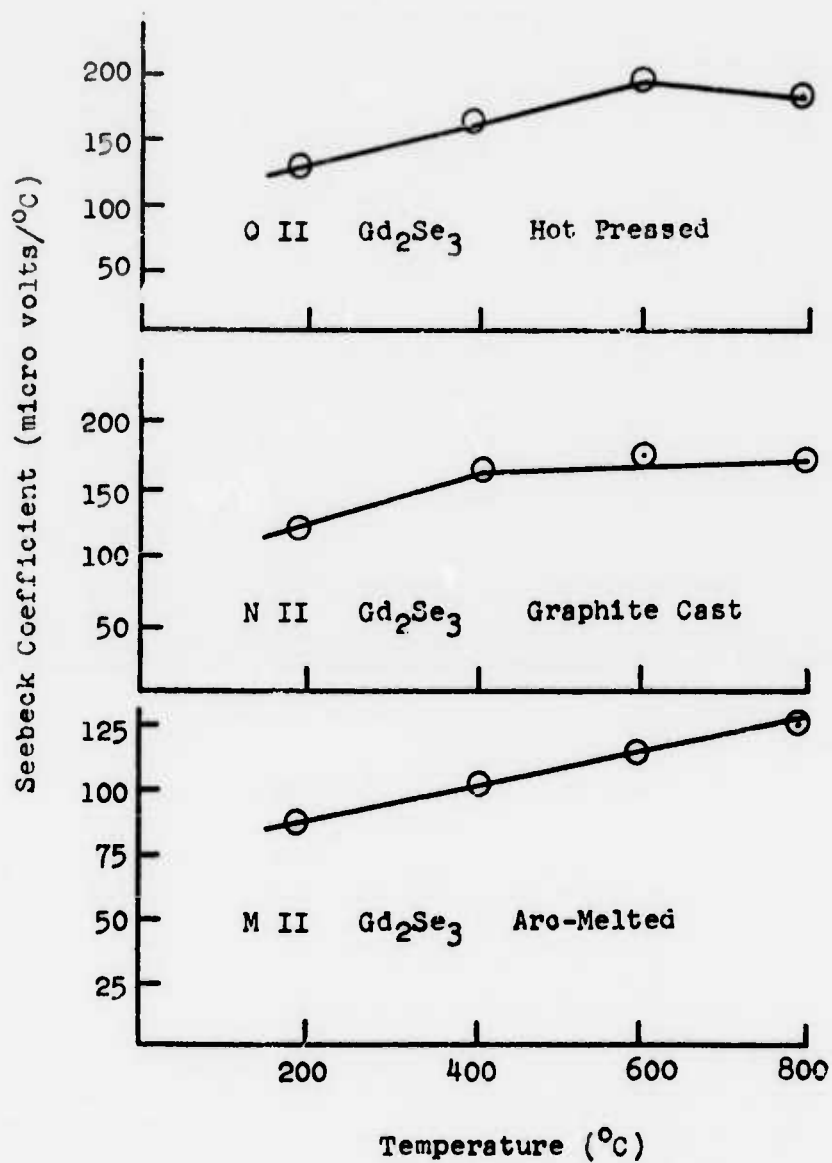


Figure 14 Effect of Processing Variables
Upon Seebeck Coefficient of Gd_2Se_3

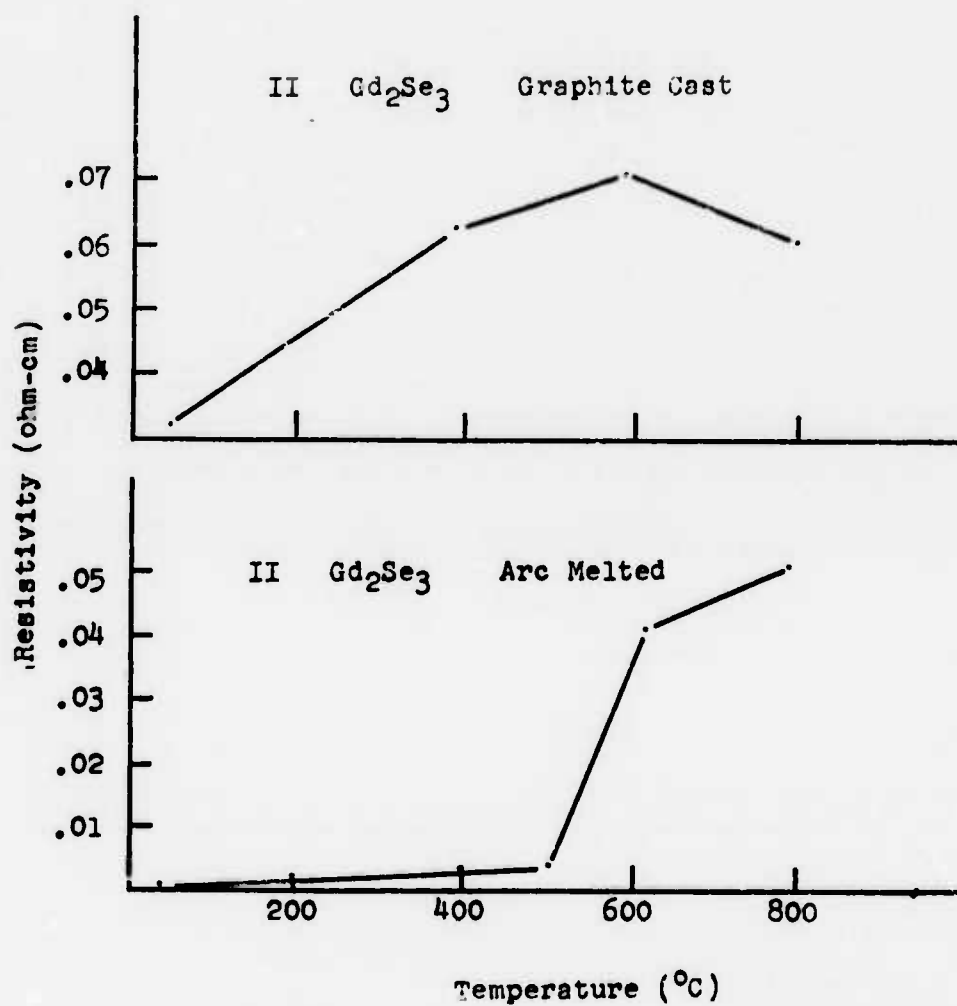


Figure 15 Effect of Processing Variables
Upon Resistivity of Gd_2Se_3

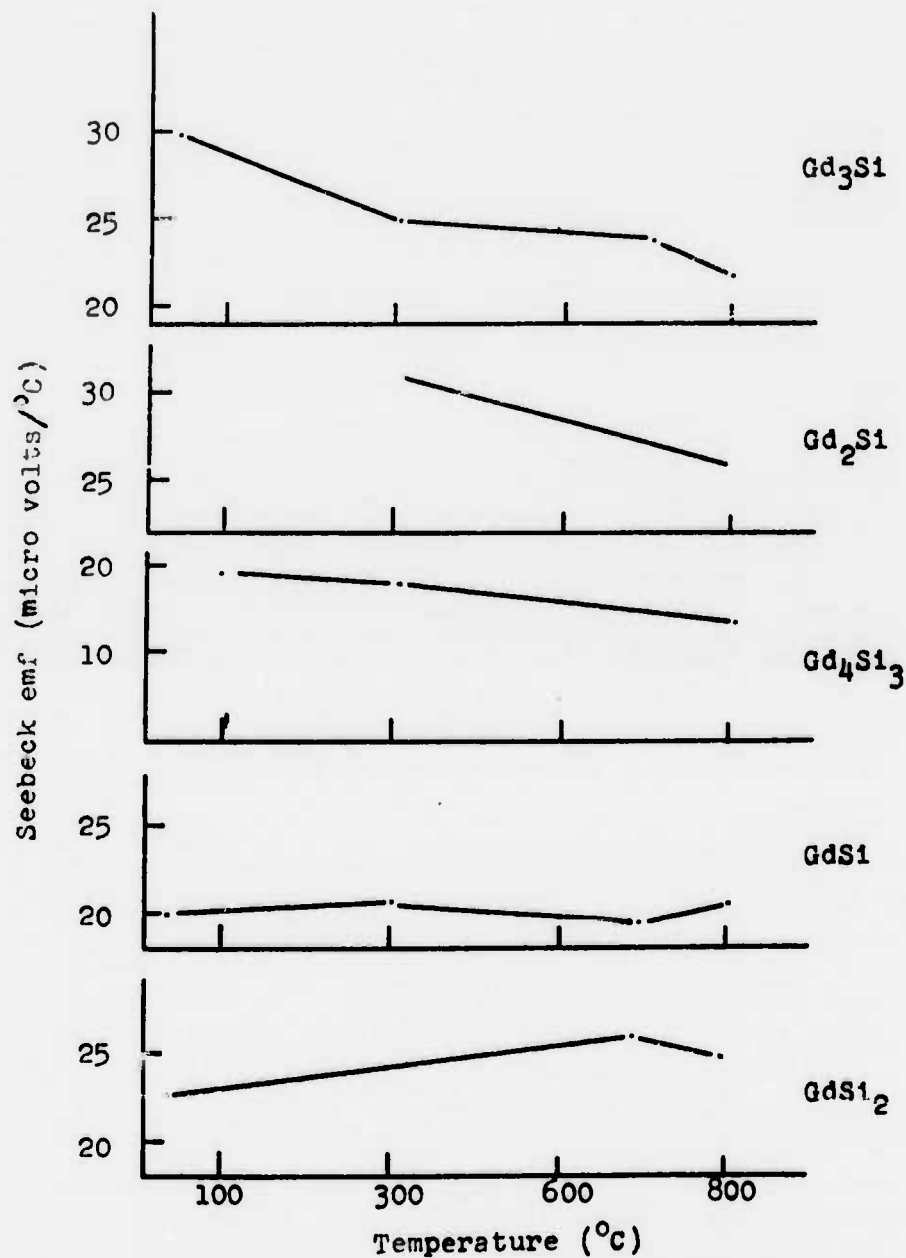


Figure 16 Gadolinium-Silicon System
Seebeck Coefficient vs Temperature

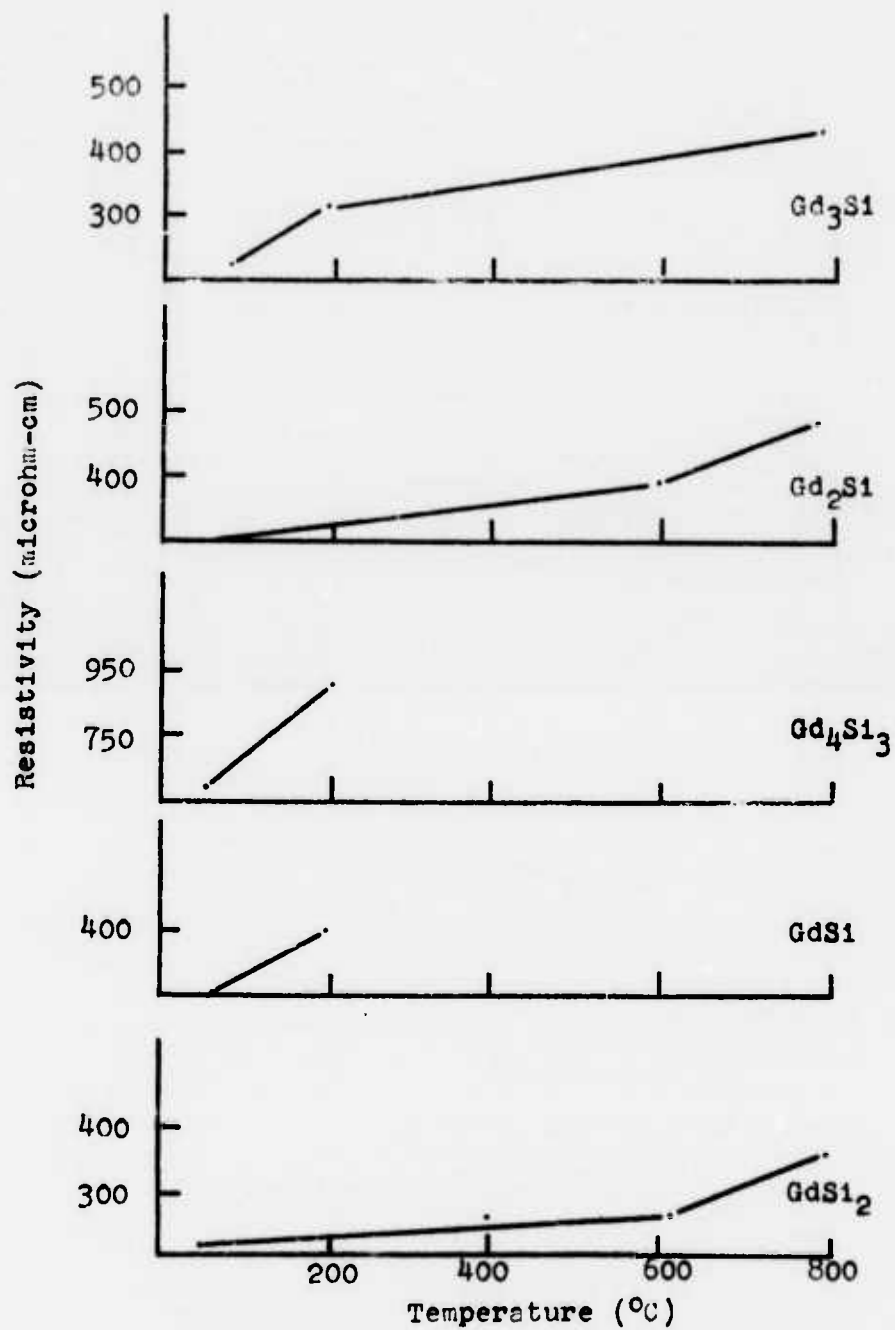


Figure 17 Gadolinium-Silicon System
Resistivity vs Temperature

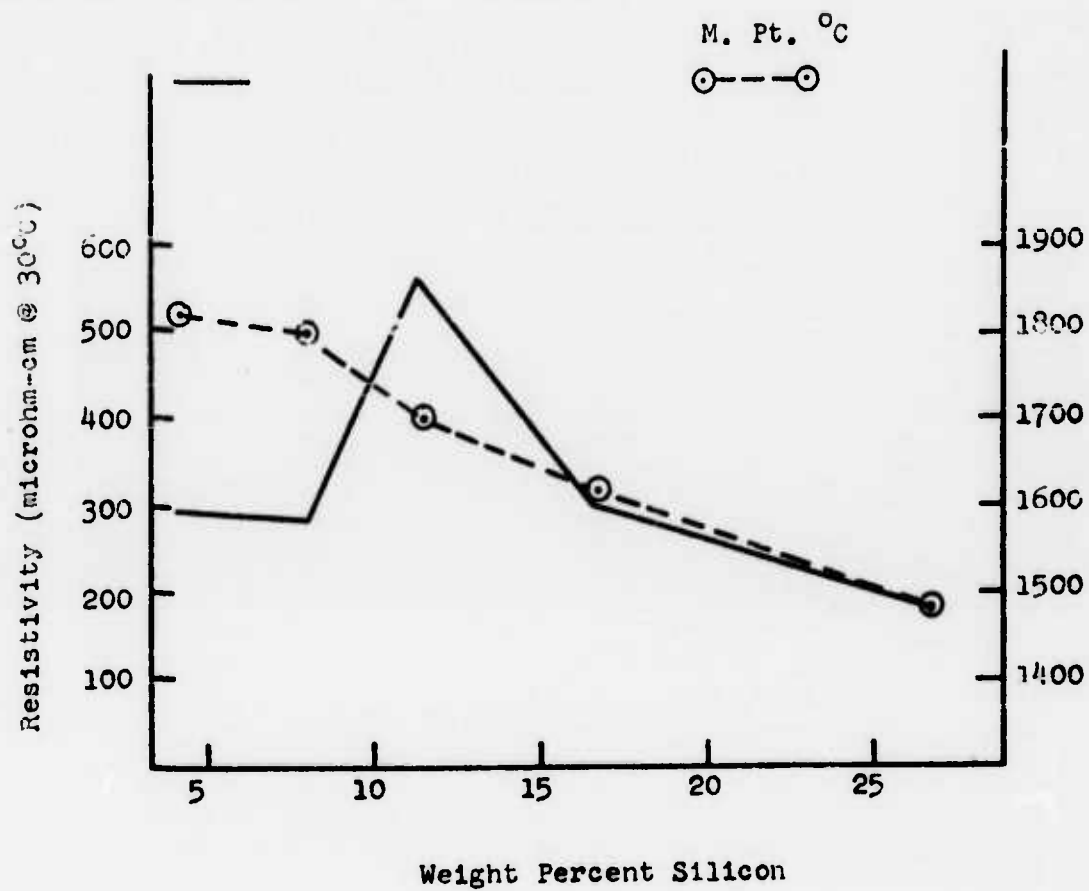


Figure 18 Gadolinium-Silicon System
Resistivity and Melting Points

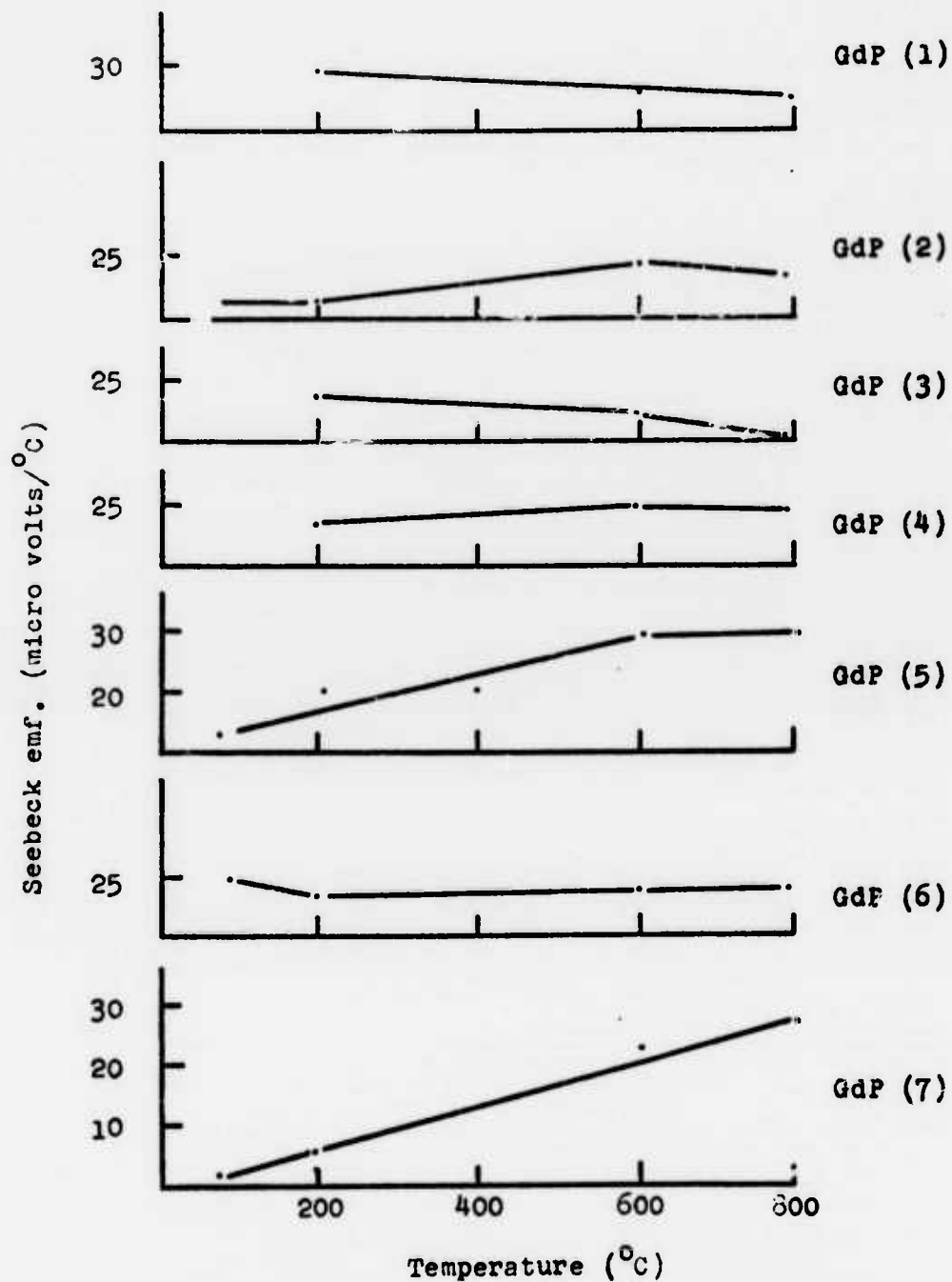


Figure 19 Gadolinium-Phosphorus System
Seebeck Coefficient vs Temperature

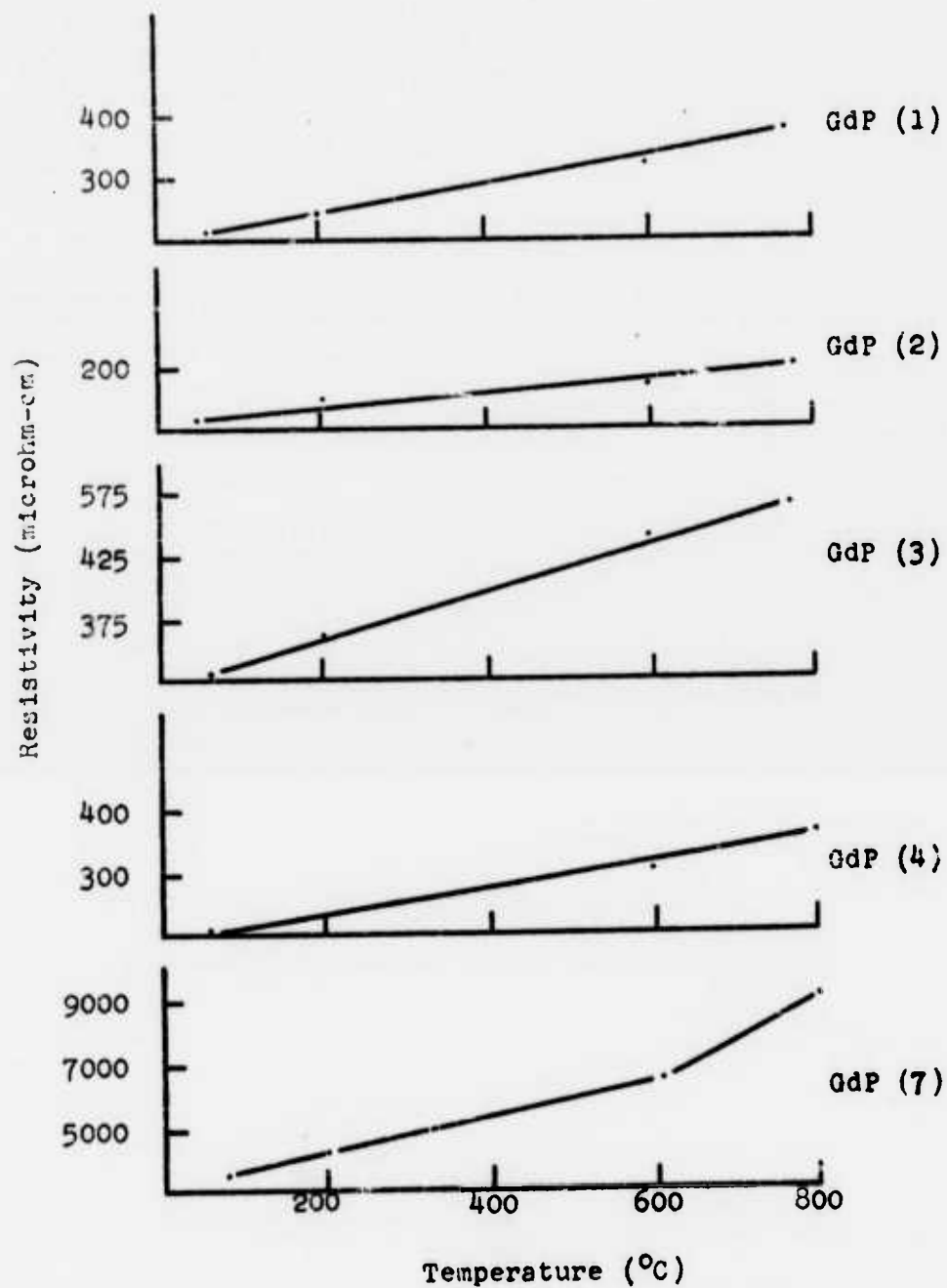


Figure 20 Gadolinium-Phosphorus System
Resistivity vs Temperature

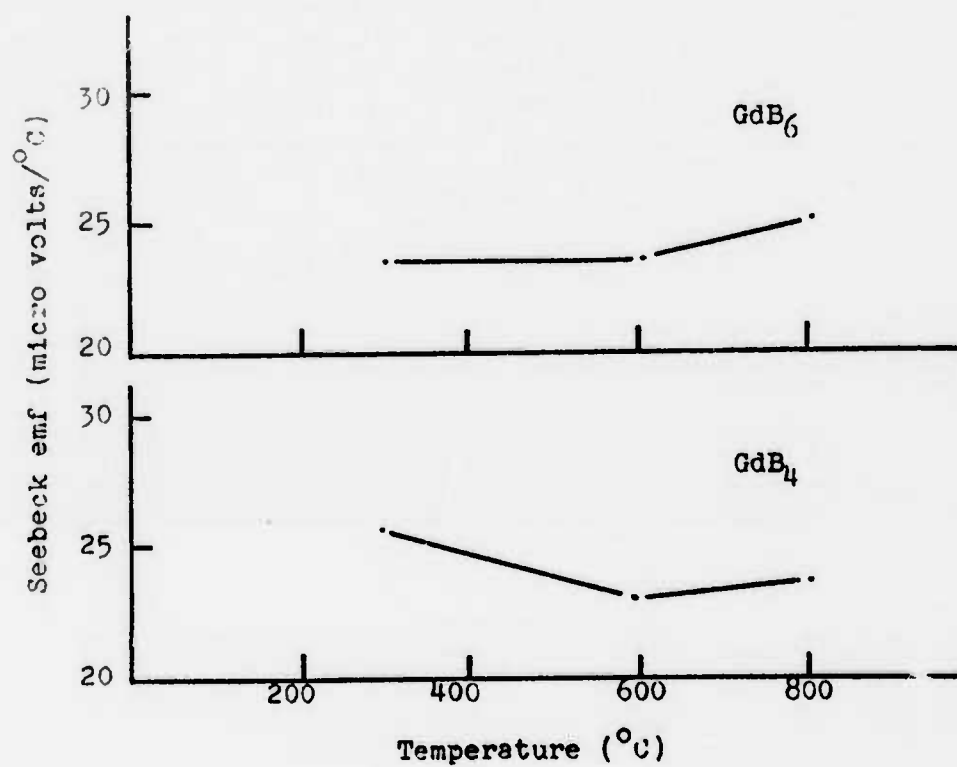


Figure 21 Gadolinium-Boron System
Seebeck Coefficient vs Temperature

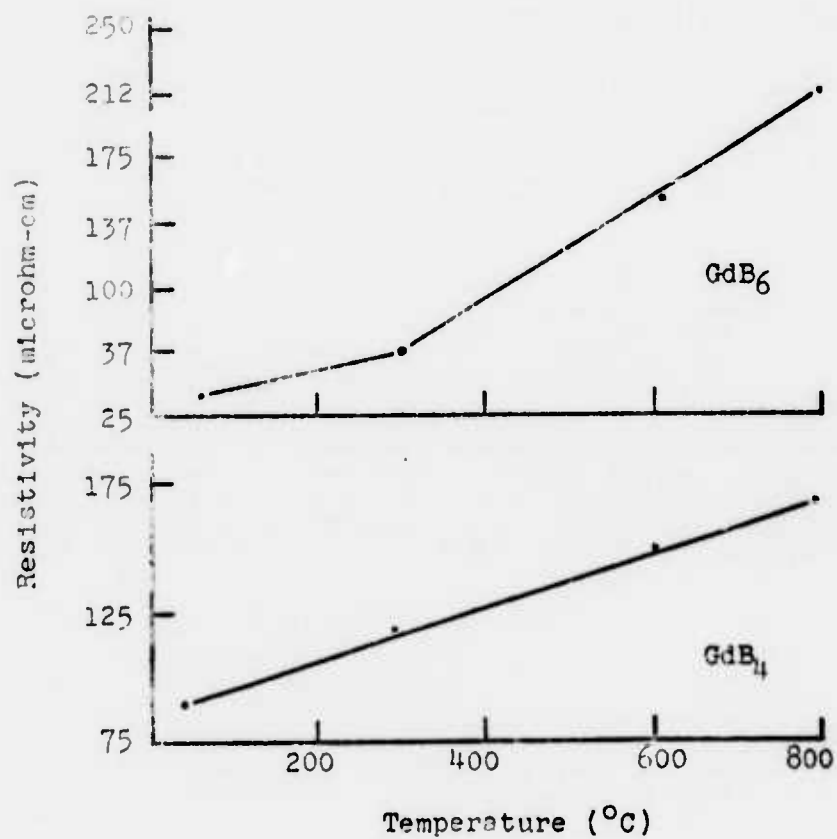


Figure 22 Gadolinium-Boron system
Resistivity vs Temperature

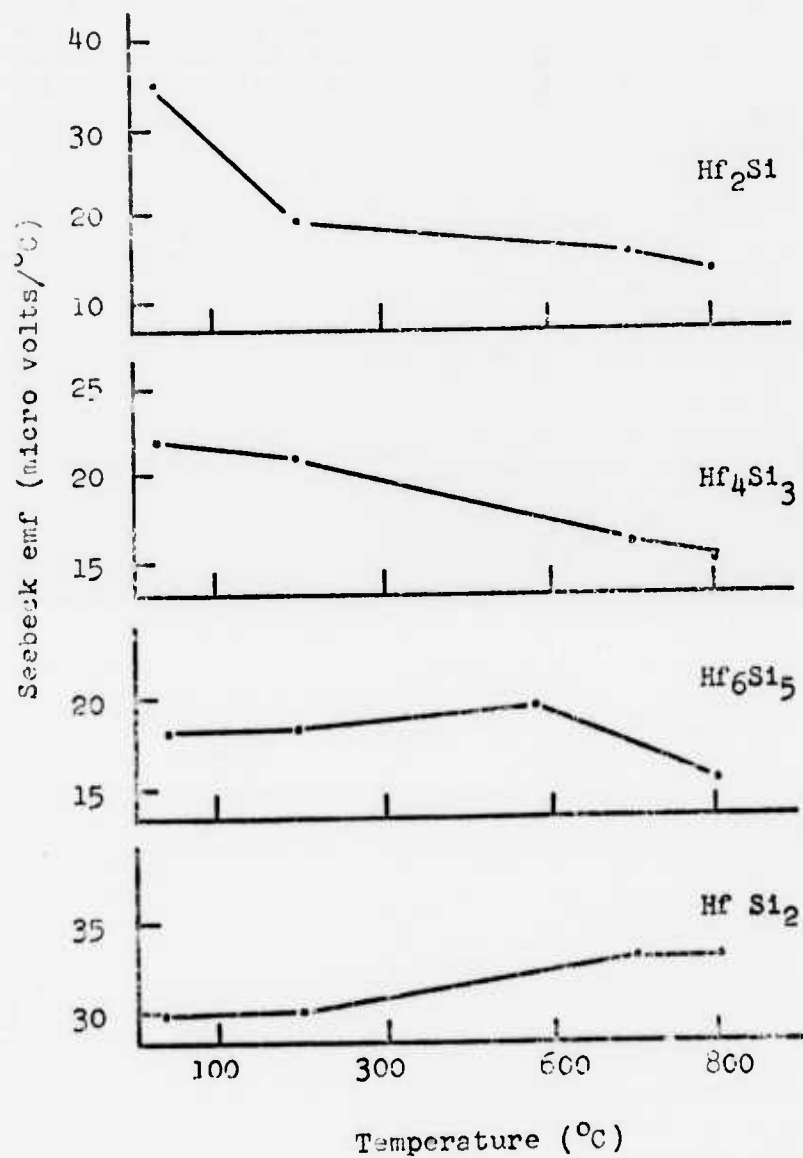


Figure 23 Hafnium-Silicon System
Seebeck Coefficient vs Temperature

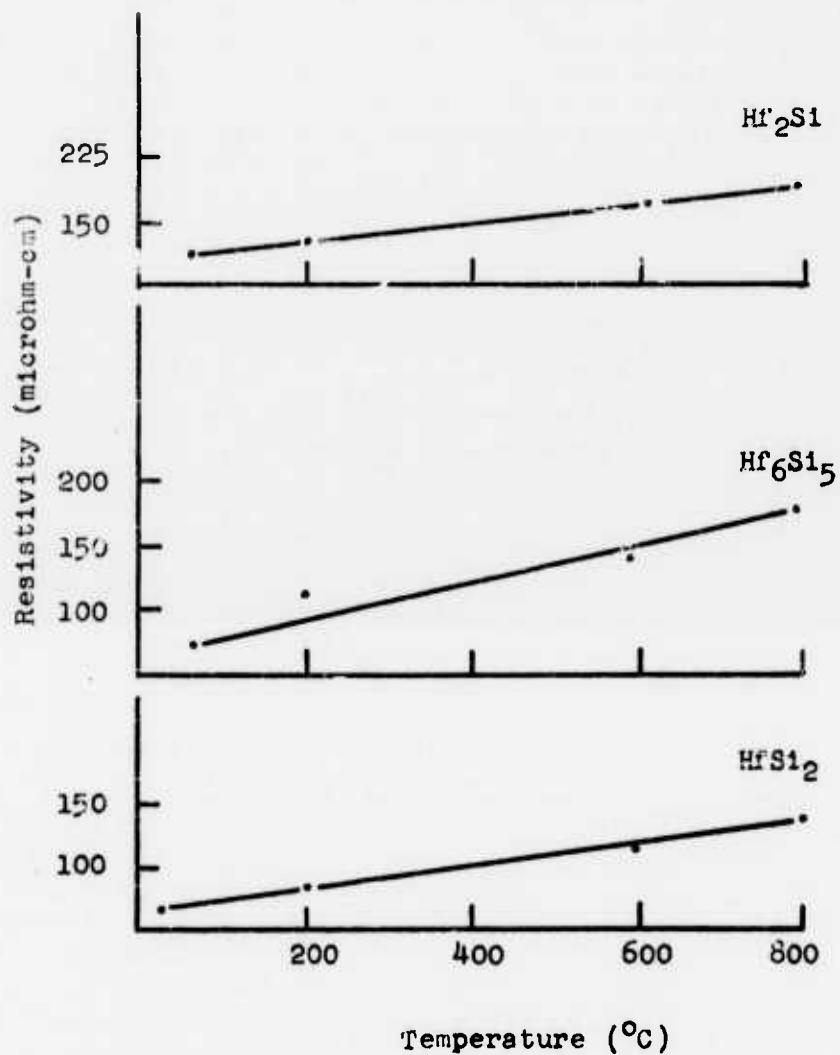


Figure 24 Hafnium-Silicon System
Resistivity vs Temperature

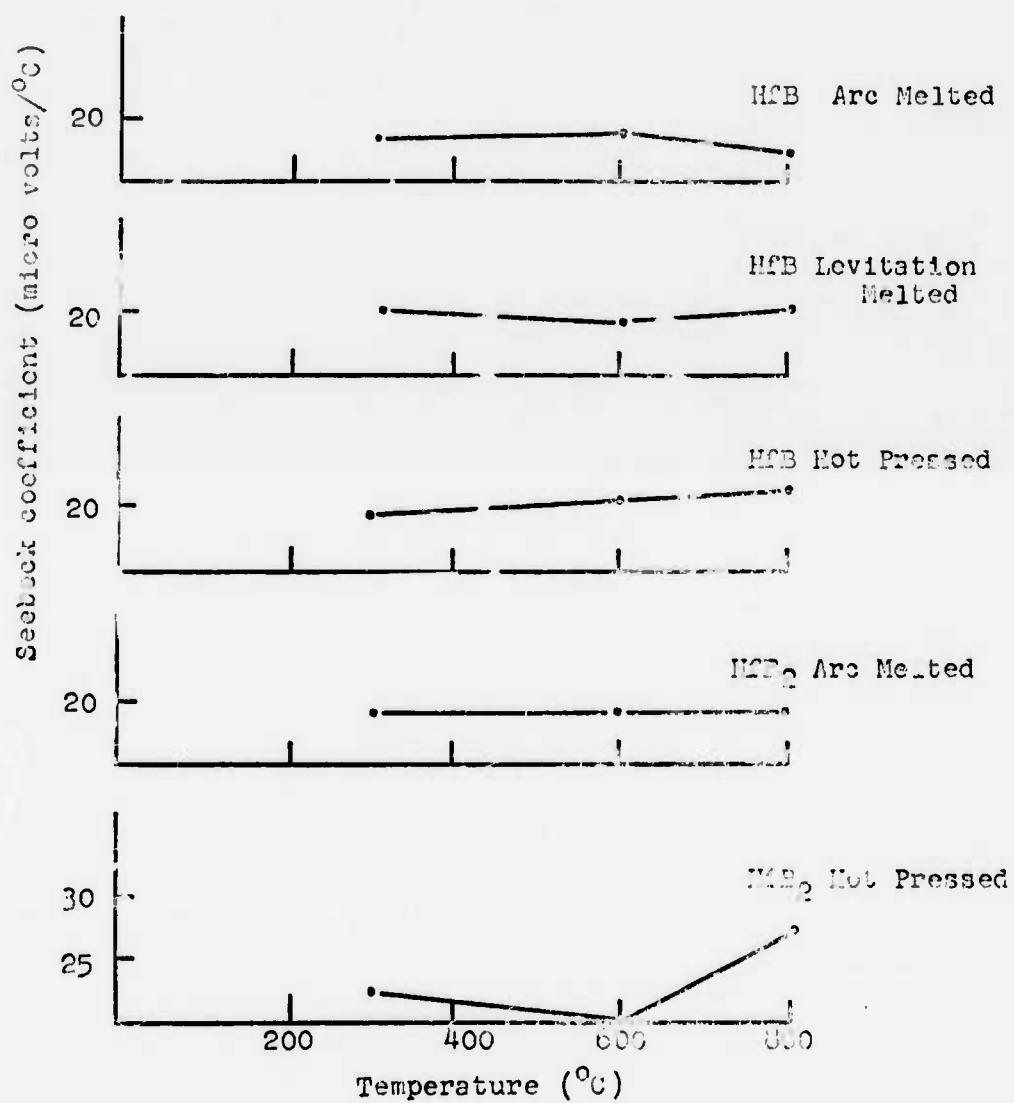


Figure 25 Hafnium-Boron System
Seebeck Coefficient
vs Temperature

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